Environmental Studies No. 48

The Flux of Suspended Particulates, Petroleum Related Hydrocarbons, Trace Metals and Nutrients from the Mackenzie River During the Winter Season: A Pilot Study of the East Channel

Northern Affairs Program

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Published under the authority of the
Hon. Bill McKnight, P.C., M.P.,
Minister of Indian Affairs and
Northern Development,
Ottawa, 1987.

QS-8398-000-EF-A1
Catalogue No. R71-19/48-1987E
ISBN 0-662-15639-0

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This report was prepared under contract for the Northern Environment Directorate, Department of Indian and Northern Affairs. The views, conclusions and recommendations expressed herein are those of the authors and not necessarily those of the Department.

Indian and Northern Affairs Canada
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SUMMARY

Water and suspended particulates were collected through the ice in the East Channel of the Mackenzie River about 30 km upstream from Kittigazuit Bay in April 1985 and early February 1986 to estimate the winter dissolved and particulate fluxes of trace metals, nutrients and petroleum related hydrocarbons to the Beaufort Sea. In February 1986 samples were also collected in the Main, Middle and Reindeer Channels to compare fluxes in the other major channels. Samples were collected using conventional discrete sampling methods as well as a new time-integrating, microprocessor controlled in situ pump.

The results obtained indicate that:

1) The Middle, Reindeer and East Channels account for all the winter flow through the Main Channel.

2) Suspended particulate loads decrease as a function of current speed and distance downstream. About 25% of the particulates by weight in the Main Channel settled out over a distance of about 100 km (between the Main Channel and outer channel sites). Mean concentrations were 5.15 $mg \cdot L^{-1}$ in the East Channel in 1986 (4.78 in 1985), 4.89 $mg \cdot L^{-1}$ in Reindeer Channel and 4.58 $mg \cdot L^{-1}$ in Middle channel.

3) Suspended particulates have a peak in size distribution between 2 and 6 µm. Virtually no particles were present greater than 16 µm in size in any channel.

4) The Sedisamp System continuous-flow centrifigue was useful for collecting large quantities of suspended solids. However, at the levels of winter SPM, its efficiency was only about 30% of filtration through a 0.4 µm membrane filter.

5) Organic carbon content of winter particulates was 4 - 8%. The particulate organic carbon: particulate organic nitrogen (POC:PON) ratios were generally 10 - 20 with some values as high as 30 in 1986 Main Channel samples. The lower values are more typical of ratios determined for oceanic plankton and recent marine sediments.

6) Winter chemical water properties on the basis of most major ions and nutrients are uniform across channel, with depth and between channels and did not vary significantly between years.

7) Concentrations of dissolved nonpolar and aromatic hydrocarbons were below detection limits for both water sampling methods (bottle samples and XAD-2 in situ sampler) as determined by UV-fluorescence, GC/FID and GC/MS analyses. Similar concentrations of nonpolar and aromatic hydrocarbons were found in particulates by bottle sample filtration and filtration during in situ sampling. Lower levels were present in the continuous-flow centrifuge samples. Qualitatively the particulate hydrocarbons were very similar although there were minor compositional differences between continuous-flow centrifuge and filtration sampling methods. These differences can be attributed to a less efficient recovery of low density material by the centrifuge. A pronounced odd carbon predominance in the higher alkanes indicated that the primary hydrocarbon source for all the particulate samples is terrestrial plant wax material.

8) Chlorinated hydrocarbons were found at low levels in dissolved and particulates phases. The only major chlorinated compounds found in the dissolved phase were alpha- and gamma-BHC, isomers of hexachlorocyclohexane. Hexachlorobenzene and traces of alpha-BHC were found in particulates.

9) Trace metals such as Cu, Cd, As, Hg, Pb and V appear to be primarily in a dissolved phase while Zn, Cr and Ni have a particulate component equal to or greater than dissolved levels. The winter river metal concentrations when compared to available Beaufort Sea data and recent data for other oceanic regions indicate that the river is a source of Cu, Ni, V, Zn, Pb and Cr. Concentrations of Cd and As are lower in the river than in shelf water, while Hg concentrations appear to be about the same.

10) Mean concentrations of nutrients were 9.0 $mmol \cdot m^{-3}$ N (as nitrate); 60 $mmol \cdot m^{-3}$ Si (as silicate) and 0.08 $mmol \cdot m^{-3}$ P (as orthophosphate). The river is therefore a source of Si; nitrate levels are similar to those in shelf water while phosphate concentrations in the river are at least an order of magnitude lower than marine concentrations.

11) The Seastar in situ sampler proved to be a reliable sampling device. With an XE-305/8-hydroxyquinoline column, quantitative extraction of dissolved Cu, Ni and Pb was obtained. Recoveries of Zn appear to be low but reproducible while Cd recoveries were low and variable.

With an XAD-2 column, extraction of PAHs and n-alkanes appears to be quantitative although a valid comparison with discrete sample results was not feasible because concentrations were near detection limits.

The in situ sampler proved to be a valuable method for sampling for trace levels of chlorinated hydrocarbons in both dissolved and particulate phases.

12) Metal results of centrifuge (Sedisamp) collected particulates in 1986 were higher than results for particulates collected by filtration in 1985.

13) A reliable estimate of the total winter flux of dissolved chemicals can be obtained by sampling the Main Channel alone. However, particulate concentrations decrease downstream. The flux of particulates calculated in the Main Channel was about 30% greater than the sum of the fluxes through the outer three major channels even though these channels account for 100% of the flow.

RÉSUMÉ

Dans le chenal (East Channel) du fleuve Mackenzie, à environ 30 km en amont de la baie Kittigazuit, on a recueilli en avril 1985 et au début de février 1986 des échantillons d'eau et de particules en suspension par prélèvement à travers la glace, dans le but d'estimer les apports, en solution et en suspension, d'oligo-éléments, d'éléments nutritifs et d'hydrocarbures dérivés du pétrole, dans la mer de Beaufort. En février 1986, on a aussi effectué des prélèvements dans les chenaux Main, Middle et Reindeer pour comparer les apports dans les principaux autres chenaux. On a recueilli les échantillons en employant des méthodes traditionnelles d'échantillonnage discret, en même temps qu'une nouvelle pompe réglée par un microprocesseur à temps intégré, utilisable pour des prélèvements in situ.

Les résultats obtenus indiquent que :

1) Les chenaux Middle, Reindeer et East canalisent tant le débit hivernal à travers le chenal Main.

2) Les charges de particules en suspension diminuent en fonction de la vitesse du courant et de la distance en aval. Environ 25 % (en poids) des particules se sont déposées dans le chenal Main sur une distance d'enviror 100 km (entre le chenal Main et des sites de chenaux périphériques). Les concentrations moyennes étaient de 5,15 $mg.L^{-1}$ dans le chenal East en 1986 (4,78 en 1985), de 4,89 $mg.L^{-1}$ dans le chenal Reindeer et de 4,58 $mg.L^{-1}$ dans le chenal Middle.

3) Les particules en suspension présentent un pic granulométrique compris entre 2 et 6 µm. On n'a rencontré pratiquement aucune particule de granulométrie supérieure à 16 µm dans un chenal quelconque.

4) Le centrifugeur Sedisamp à débit continu a permis de prélever des quantités importantes de solides en suspension. Toutefois, aux taux hivernaux de matières particulaires en suspension (MPS), le rendement ne correspondait qu'à environ 30 % du taux de filtrage à travers un filtre à membrane de 0,4 µm.

5) En hiver, le taux de carbone organique des particules était de 4 à 8 %. Les rapports carbone organique particulaire : azote organique particulaire (POC:PON) se situaient généralement entre 10 et 20, avec des pointes de 30 dans des échantillons prélevés en 1986 dans le chenal Main. Les valeurs moindres sont plus typiques des rapports déterminés pour le plancton océanique et les sédiments marins récents.

6) Les propriétés chimiques de l'eau en hiver, déterminées d'après la concentration de la plupart des principaux ions et éléments nutritifs, sont uniformes sur la largeur des chenaux, sur toute leur profondeur, et dans tous les chenaux, et n'ont pas varié d'une année à l'autre.

7) Les concentrations des hydrocarbures en solution, non polaires et aromatiques, se sont situées dessous des limites de détection, lorsqu'on a employé les deux méthodes d'échantillonnage de l'eau. (échantillonnage dans des bouteilles et échantillonneur in situ XAD-2); pour effectuer les dosages, on a utilisé les procédés suivants : fluorimétrie UV, CG/DIF et CG/SM. On a constaté l'existence de concentrations similaires d'hydrocarbures non polaires et aromatiques dans des particules recueillies par filtrage d'échantillons en bouteilles et filtrage effectué durant l'échantillonnage in situ. On a observé des concentrations moindres dans les échantillons prélevés avec le centrifugeur à débit continu. D'un point de vue

qualitatif, les hydrocarbures en suspension étaient très semblables, mais on a toutefois observé que des différences mineures de composition existaient entre les produits recueillis avec le centrifugeur à débit continu et ceux prélevés par filtrage. On peut attribuer ces différences à un plus faible taux de récupération des produits de faible densité par le centrifugeur. Une nette prédominance d'un nombre impair d'atomes de carbone dans les alcanes supérieurs a indiqué que la principale source d'hydrocarbures dans tous les échantillons de particules en suspension était la cire provenant de plantes terrestres.

8) On a trouvé de faibles taux d'hydrocarbures chlorés, dans les phases en solution et en suspension. Les seuls composés chlorés importants découverts dans la phase en solution étaient l'hexachlorobenzène alpha et l'hexachlorobenzène gamma, isomères de l'hexachlorocyclohexane. On a découvert dans les particules en suspension de l'hexachlorobenzène et des traces d'hexachlorobenzène alpha.

9) Il semble que les oligo-éléments métalliques tels que Cu, Cd, As, Hg, Pb et V soient principalement présents à l'état dissous, tandis que Zn, Cr et Ni sont autant ou davantage présents dans des produits en suspension qu'à l'état dissous. En hiver, les concentrations d'éléments métalliques dans l'eau fluviale, comparativement aux résultats disponibles pour la mer de Beaufort et aux données récentes obtenues pour d'autres régions océaniques indiquent que le cours d'eau est une source de Cu, Ni, V, Zn, Pb et Cr. Les concentrations de Cd et As sont plus basses dans les eaux fluviales que dans les eaux marines de la plate-forme continentale, tandis que les concentrations de Hg ne semblent pas varier.

10) Les concentrations moyennes d'éléments nutritifs étaient de 9,0 mmol.m^{-3} N (sous forme de nitrates); de 60 mmol.m^{-3} Si (sous forme de silicates) et de 0,08 mmol.m^{-3} P (sous forme d'orthophosphates). Par conséquent, le cours d'eau est une source de Si; les concentrations de nitrates y sont les mêmes que dans les eaux marines de la plate-forme continentale, tandis que les concentrations de phosphates y sont d'au moins un ordre de grandeur inférieures aux concentrations mesurées dans les eaux marines.

11) L'échantillonneur in situ Seastar s'est avéré très fiable. Avec une colonne d'extraction par le 8-hydroxyquinoline, de type XE-308, on a effectué l'extraction quantitative de Cu, Ni et Pb dissous. Le taux d'extraction de Zn paraît faible, mais il est reproductible, tandis que les taux d'extraction de Cd sont faibles et variables.

Lorsqu'on emploie une colonne d'extraction de type XAD-2, l'extraction des HPA (hydrocarbures polyaromatiques) semble être quantitative, mais on n'a pu faire de comparaison avec les résultats obtenus sur des échantillons discrets, les concentrations étant proches des limites de détection.

La méthode de l'échantillonneur in situ s'est avérée utile pour l'échantillonnage de concentrations minimes d'hydrocarbures chlorés à la fois dans les phases dissoutes et les phases en suspension.

12) Les concentrations de métaux, msurées en 1986 dans des produits particulaires recueillis par centrifugation (centrifugeur Sedisamp) étaient plus élevées que celles mesurées dans des produits du même type recueillis par filtrage en 1985.

13) En effectuant dans le chenal principal (Main Channel) seul des prélèvements, on peut obtenir une estimation fiable du débit total des produits chimiques dissous. Cependant, les concentrations de particules diminuent en aval. Le débit de particules, tel que calculé dans le chenal principal (Main Channel) était d'environ 30 % supérieur à la somme des débits traversant les trois principaux chenaux, alors que ces derniers canalisent 100 % du débit.

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UNITS

The International System of Units (SI) has been used wherever possible. Exceptions in the use of SI are classes of compounds which comprise a number of different molecules (e.g., PAHs, n-alkanes, PCBs). The International Union of Pure and Applied Chemistry (IUPAC) endorses the exclusive use of SI units for chemical quantities. Historical data however have traditionally been expressed in ppm or ppb. Factors to convert from these units to SI units are given below:

Chemical Quantity	To convert from	to	Multiply by
aluminum	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	37.06
arsenic	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	13.33
	$\mu g \cdot g^{-1}$	$mol \cdot kg^{-1}$	13.33
barium	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	7.28
calcium	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	24.95
cadmium	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	8.90
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	8.90
chloride	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	27.82
copper	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	15.74
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	15.74
chromium	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	19.23
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	19.23
fluoride	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	52.26
iron	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	17.91
lead	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	4.83
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	4.83
magnesium	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	41.14
manganese	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	18.20
mercury	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	4.99
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	4.99
nickel	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	17.03
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	17.03
nitrate	$\mu g.at/L$	$mmol \cdot m^{-3}$	1

phosphate	µg.at/L	$mmol \cdot m^{-3}$	1
potassium	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	25.58
silicate	µg.at/L	$mmol \cdot m^{-3}$	1
sodium	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	43.5
sulphate	$mg \cdot L^{-1}$	$mmol \cdot m^{-3}$	10.41
vanadium	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	19.63
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	19.63
zinc	$\mu g \cdot L^{-1}$	$\mu mol \cdot m^{-3}$	15.3
	$\mu g \cdot g^{-1}$	$\mu mol \cdot kg^{-1}$	15.3

ACKNOWLEDGEMENTS

Several individuals within Arctic Laboratories and in other organizations contributed time and resources to this study. Trace metal analysis were carried out by Krystyna Gorzelska, Vivian Mozol and Trevor Smyth. Sediment trace metals were analyzed by Kathy McIntosh and James Budac. Organic analyses were done by Dave Hope and Val Scott. Brenda Fraser drafted all diagrams; Gerrie Hosick and Irene Stevenson word processed the manuscript.

Herb Woods and staff of the Inland Waters Directorate office in Inuvik were extremely helpful in doing discharge measurements at each sampling site. Dave Sherstone, John Ostrick and Manuel Bosch of the Inuvik Research Centre, Inuvik, provided lab space and assistance with current meter and sampler recovery in March 1986. Art Barnes, NWT Highways in Inuvik, arranged for clearing tracks across the ice on the main ice roads.

John Moen of DIAND, Ottawa, assisted in the field program in February 1986. Trudy Forbes at the Pacific Geoscience Centre in Sidney, B.C. carried out Sedigraph analysis of particulates. Particulate organic carbon and nitrogen analyses were done by Kazuo Iseki at Ocean Chemistry Division, Institute of Ocean Sciences, Patricia Bay, B.C.

Camille Mageau, DIAND, Ottawa was the contract manager for the study.

1. INTRODUCTION

The Mackenzie River drains an area of about 1.8×10^6 km^2 and is North America's largest north-flowing river (Figure 1.1). The estimated annual flow of 3.7×10^{11} m^3 (Thomas et al., 1983) discharges into the Beaufort Sea through a large delta and is the major influence on the oceanography and sediment properties of the Beaufort Sea shelf. An understanding of the natural sediment and chemical loads carried by the Mackenzie River is necessary to predict and assess the environmental impact of future developments on the delta, shelf area and waters of the Beaufort Sea. The loads considered important with respect to possible developments are suspended solids (hence sediment transport) and environmentally important chemical parameters such as petroleum related hydrocarbons, trace metals and nutrients. At present there is little information available on these constituents or on their seasonal nature in the shelf areas; and that which is available points to the importance of determining the flux of the Mackenzie River.

Suspended solid loads carried by the Mackenzie River are thought to have a major bearing on the sedimentation rates on the Beaufort Sea shelf. These inputs have been estimated to comprise approximately 97% of the annual sediment flux to the Beaufort Sea (Thomas et al., 1983). Data on sedimentation rates, the nature of the loads and their seasonal variability have a twofold relevance - one being the associated engineering problems, and the other, environmental. In terms of present-day engineering problems, transport processes and sedimentation rates are required in order to assess the probability of siltation, both in the river channels and on the shelf, in pipeline trenches, and in bottom structures such as 'glory holes' or ice scours. In areas such as the Mackenzie Trough, these parameters have a bearing on determining seabed stability characteristics (e.g., slope instability and slumping).

The corollary sediment/water chemistry (particulate and dissolved) of environmentally important parameters is not well known, in part because of sampling and analytical difficulties. Earlier compilations (see for example Reeder et al., 1972, Mackenzie River Basin Committee, 1981) provided little meaningful data. Some of these values were suspect due to potential contamination; some were at or below detection limits which are now considered insensitive for unpolluted river systems. Recent attempts to derive a gross budget for chemical inputs to the Beaufort Sea shelf have been limited chiefly by uncertainties regarding the input of the Mackenzie River (Thomas et al., 1983). These uncertainties are compounded by the large seasonal variation in discharge and the character of the sediment load (variations in

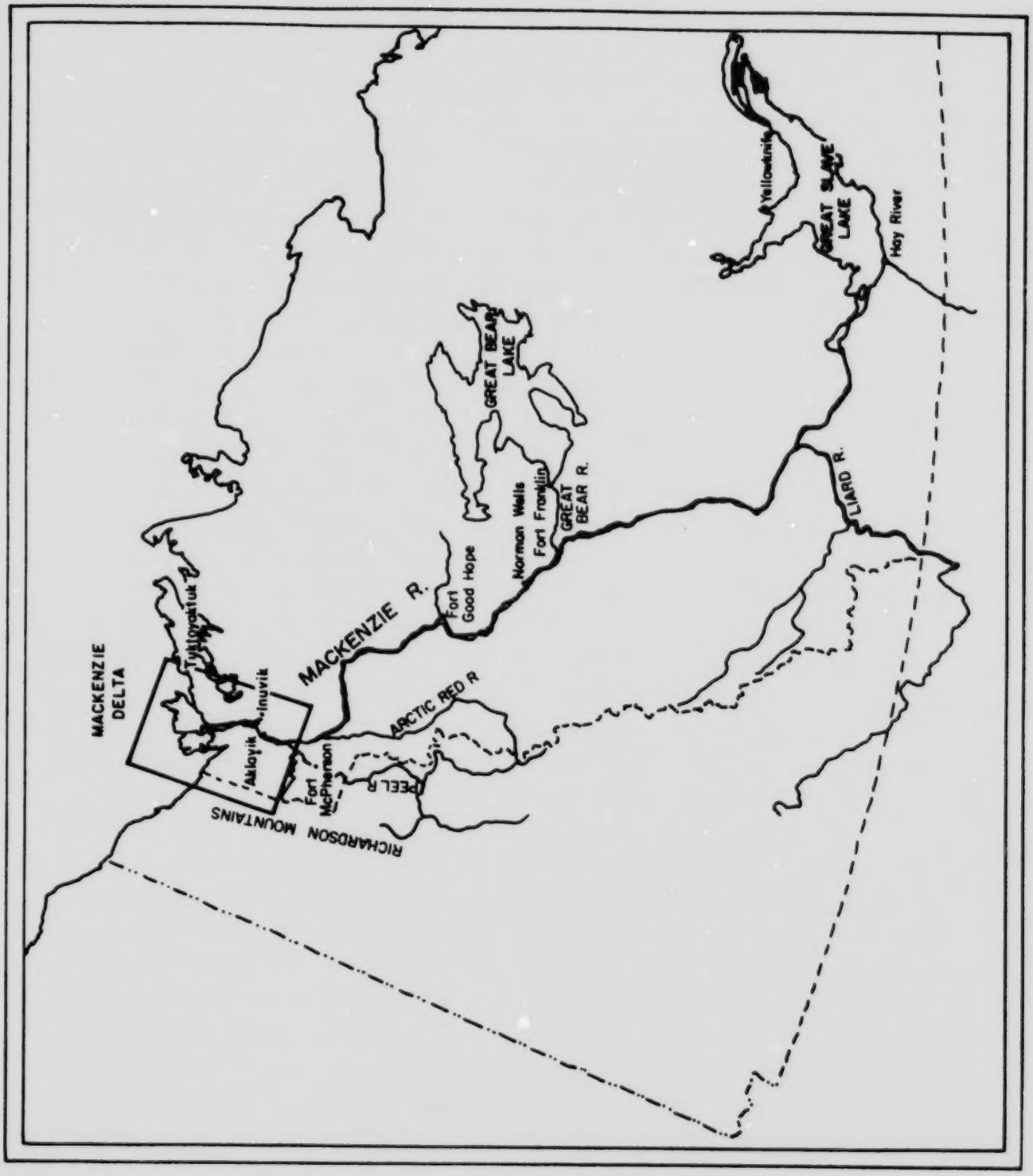


Figure 1.1 The Mackenzie River Basin and Delta

annual flow at Arctic Red River are shown in Figure 1.2). Seasonal fluctuations, especially the contrast between freshet and quiescent conditions, are expected to add at least an order of magnitude to variation in the chemical as well as the suspended particulate loading.

The objectives of this study were to:

1. determine the feasibility of conducting a detailed sampling program in the winter months in the Mackenzie River Delta;

2. provide a time series of measurements of river discharge, sediment discharge, suspended sediment concentrations and detailed information on suspended particulate grain size distributions characterizing the winter flow regime of the East Channel of the Mackenzie River prior to entry into the Beaufort Sea;

3. provide a concurrent time series of dissolved and particulate petroleum related hydrocarbons, trace metal and nutrient element concentrations;

4. evaluate the use of a moored in situ sampler for collecting time-integrated values for metals, hydrocarbons and SPM.

Study of the winter flow regime through the East Channel of the Mackenzie River was proposed for a number of reasons: 1) East Channel input has a direct impact on Kugmallit Bay, an area of current exploration and development; 2) there is ease of access afforded by the ice road between Inuvik and Tuktoyaktuk; and 3) although the discharge is much greater in the late spring and summer, the winter flow is expected to be more uniform and therefore more amenable to a preliminary survey. The study was intended to demonstrate the feasibility of collecting data through the difficult winter months and to employ the data to extrapolate into the summer regime (high and variable runoff) and for other channels which flow into the Beaufort Sea. The winter flow regime (i.e. ice covered water) persists for approximately half the year and has been estimated to account for 44% of the total annual river discharge (Thomas et al., 1983). Although the winter particulate flux is expected to be only a few percent of the annual particulate flux, the winter flux of dissolved metals and hydrocarbons should be a significant portion of the annual total. In addition, dissolved metal and hydrocarbon concentrations should be higher in winter

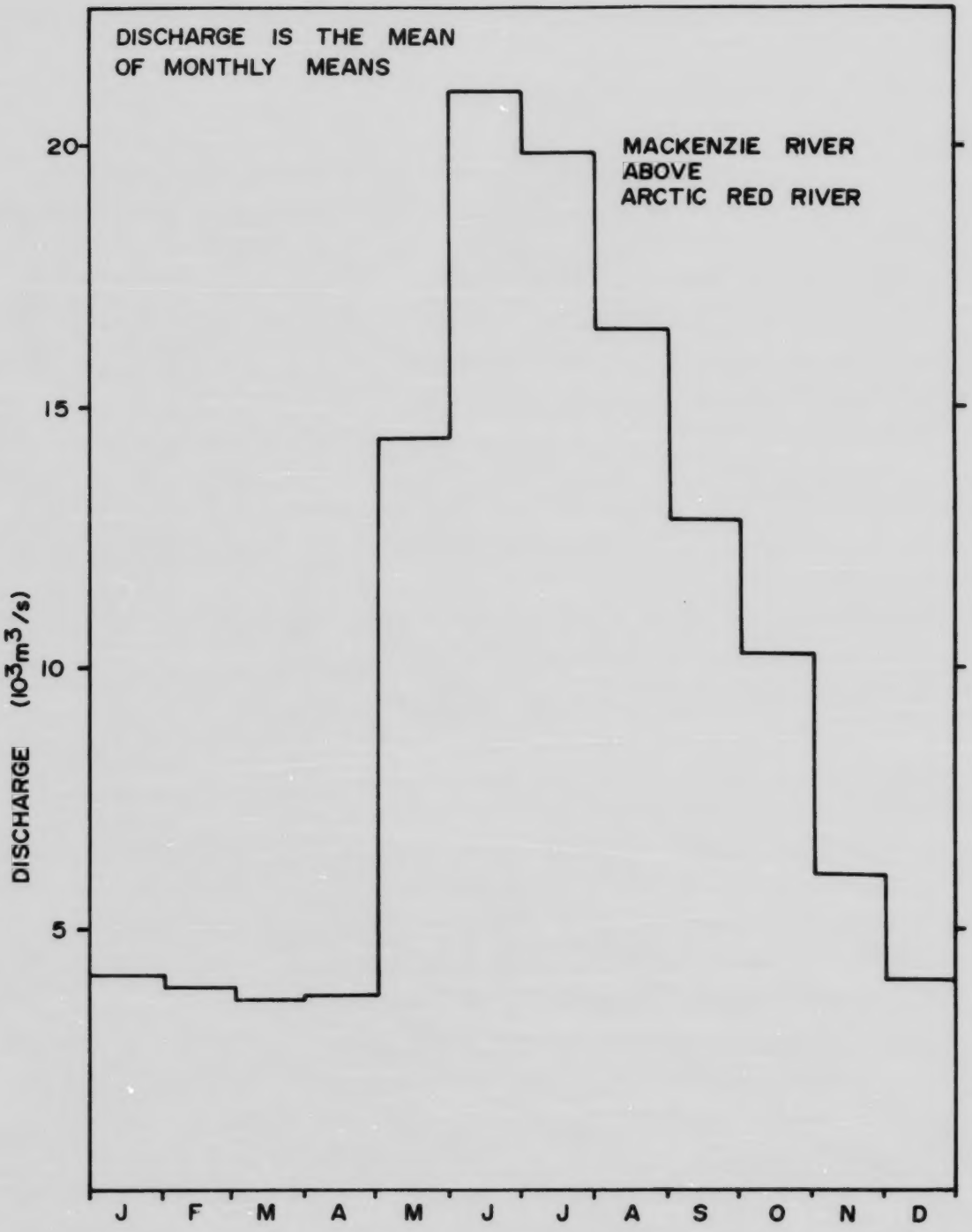


Figure 1.2. Monthly mean discharge of the Mackenzie River at Arctic Red River
Source: Mackenzie River Basin Committee (1981).

as concentrations vary inversely with flow in most rivers (Forstner and Wittmann, 1979). The dissolved fraction is certainly the most environmentally labile and therefore the winter flux will be important on an annual basis in terms of environmental impact.

Water from the Mackenzie River enters the Beaufort Sea through a number of channels over a wide front. Little is known about the flows in the various channels and methods for chemical sampling have not as yet become standardized or routine. Sampling all major channels is a difficult task logistically which is further complicated in winter by freezing conditions. The usual sampling procedure for trace metals and hydrocarbons involves taking discrete samples at a single point in time. Detailed sampling is therefore very labour intensive and costly. Where average results are needed over a long time period, a large number of analyses are required.

The Seastar in situ water sampling system is a recent advance in water sampling for trace organics and trace metals (Green et al., 1986). The system consists of a microprocessor-controlled pump which draws water through an attached Teflon extraction column filled with a resin suitable for either organics or metals. The volume of water sampled is measured with a flow meter and displayed on a liquid crystal display (LCD) on the top of the pressure housing. A Teflon filter housing for a 142 mm diameter filter is used to remove particulates before the columns. Because water is pulled though the columns, contamination possibilities from the pump are eliminated. Handling in the field is also simplified and storage problems are overcome. The method provides a time-integrated sample rather than an instanteous sample which has the advantage that short term fluctuations are averaged out. In situ sample processing is another attraction for monitoring in remote locations by obviating the need to transport large volumes of water. Very large volumes can be processed; up to 1000 L can be filtered and extracted. The microprocessor control allows long mooring periods; almost any combination of pump on/off cycle can be programmed, allowing sampling to be done over a long period (up to a month or more). The in situ samplers however, have not been field tested in a winter river environment. An objective of this study was to test the effectiveness of an in situ sampler approach to the collection of metal and hydrocarbon data.

2. METHODS

2.1 Sampling

2.1.1 Strategy

The original goal of the sampling program was to provide a time series of samples which were representative of the chemical flux and the sediment loading being transported to the Beaufort Sea by the East Channel of the Mackenzie River during the winter months. Since there is no means to verify that samples are indeed representative without collecting a prohibitively large number of samples, the proposed sampling strategy was formulated based on certain assumptions regarding the river flow and channel characteristics. The location and size of the river, as well as the season, impose practical constraints on sampling frequency and the number of locations. The assumptions made were:

1. river flow is relatively uniform during the winter;

2. short term variations in flow (less than 1 month) are not significant;

3. at the selected site, the river is hydraulically smooth;

4. parameters measured at this site are indicative of the input of the East Channel into the Beaufort Sea.

The number and location of the vertical profiles (verticals) determine the accuracy with which the total discharge can be estimated. At least 20 verticals with two or three measurement points in each appear to be sufficient for a reliable determination of the mean velocity. This approach generally allows an error in the discharge estimation of 2.5 - 3% (Jansen et al., 1979) and is the method used by Inland Waters Directorate (IWD) for their discharge measurements. However, arctic winter conditions and sampling off an ice road (high embankments) with temperature sensitive, scientific equipment imposes constraints upon chemical sampling and its frequency. Although 20 verticals are recommended for an accurate discharge measurement, decreasing the number of verticals to 10 results in only a minor absolute decrease in accuracy (ca. 4 - 5% in discharge, Jansen et al., 1979).

Less frequent sampling produces geometrically higher errors. This is reasonable when the true scale (i.e., no vertical exaggeration) of a channel cross section is considered. For chemical sampling, it was felt that the largest sources of variability were likely to be in sampling, handling and analysis if the river were well mixed. Therefore fewer verticals were sampled but duplicate or triplicate samples at each vertical/depth were taken. In 1985, 5 verticals were sampled for metals, hydrocarbons and nutrients.

To meet the primary study objectives, both particulate and dissolved samples were taken along with sufficient supporting data to characterize the water, suspended sediment and river discharge. A summary of the study variables is given in Table 2.1.

2.1.2 Sampling Frequency

Three site visits were proposed originally, all in 1985: 1) early January; 2) early March; and 3) late April. The proposed frequency was based on the assumption that short term temporal (daily, weekly) variations during this period would be relatively minor. However, only the April 1985 trip was possible. The in situ sampler was moored for a period of a few days rather than a month or more as intended. Sampling in April 1985 (Figure 2.1) indicated that water properties at the sampling site were uniform across channel and with depth and that fewer samples would suffice for estimating the mean concentration of all parameters. As a result, the 1986 sampling strategy was modified to reflect this information and to try and address the broader objectives of examining the total discharge of the Mackenzie River. Therefore, 1986 sampling was undertaken only once but at four sites instead of just one (Figure 2.2). The 4 sites were:

a) East Channel site previously sampled in 1985;

b) Middle Channel downstream from Tununuk near Harry Channel;

c) Reindeer Channel; and

d) the Main Channel on the ice road to Aklavik just above Napoiak Channel.

Three verticals at each site were sampled for trace metals, nutrients and hydrocarbons instead of 5. Verticals were at mid-points in the channel and

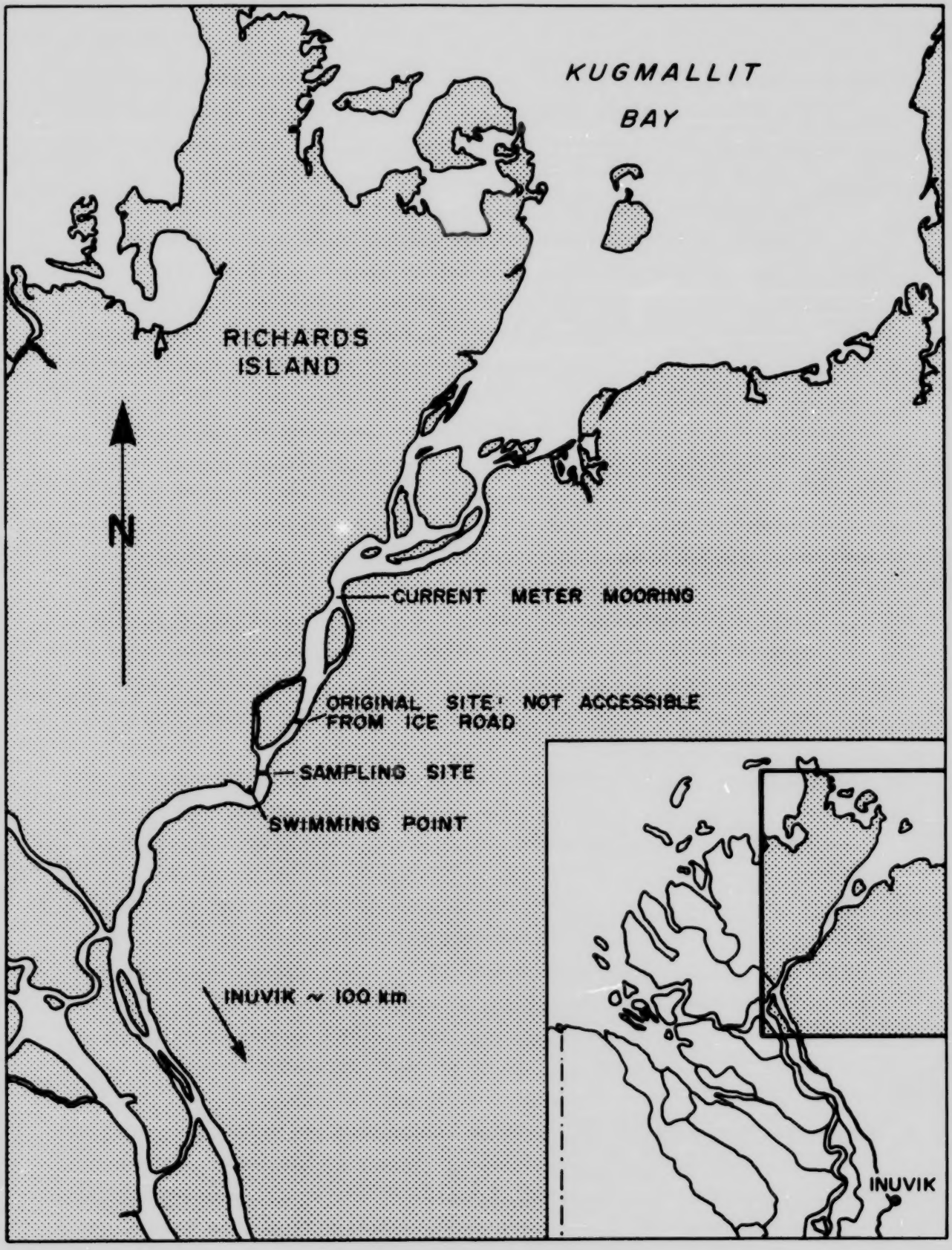


Figure 2.1. Sampling Sites, April 1985.

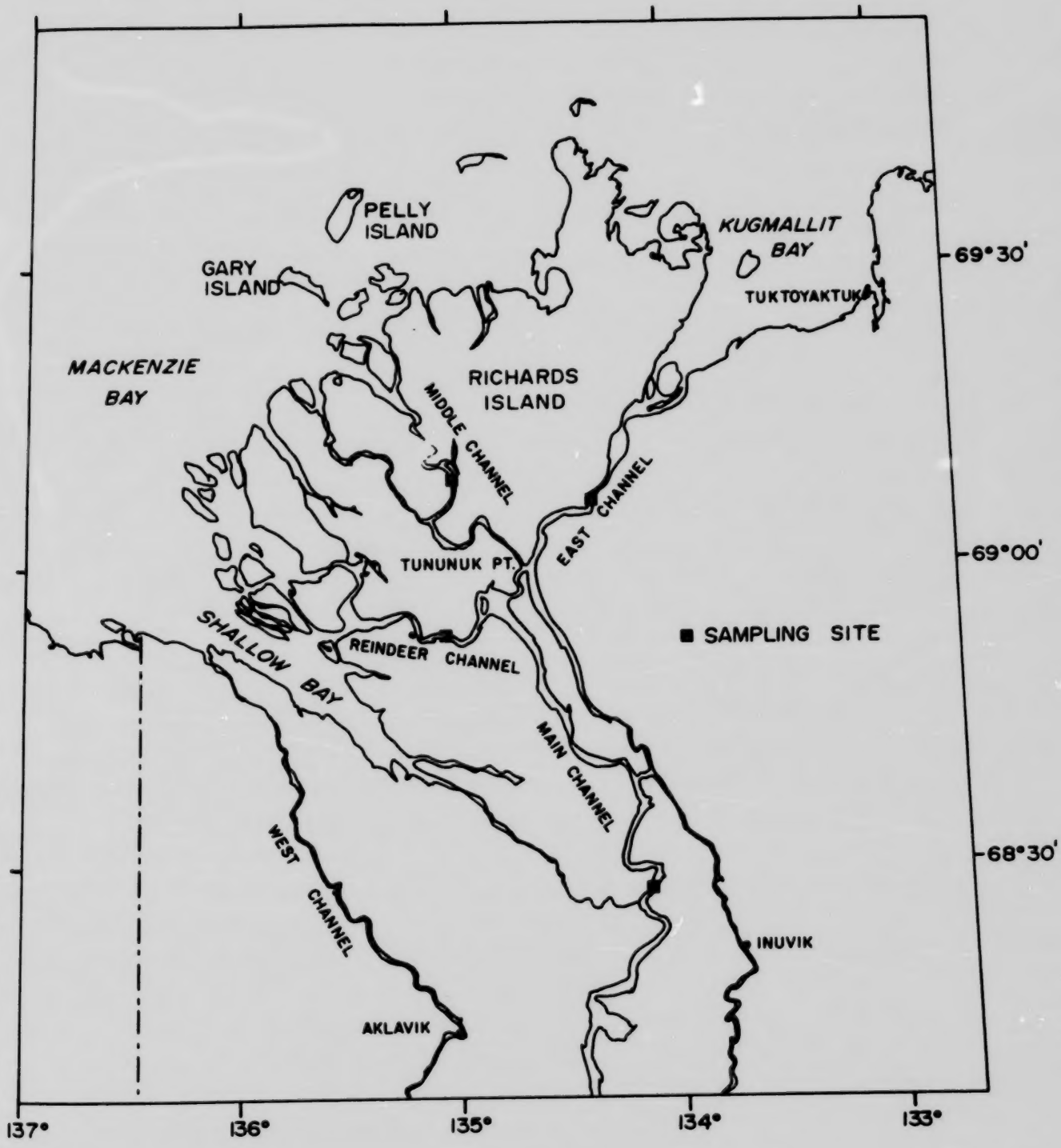


Figure 2.2. Sampling Sites, February 1986.

Table 2.1.

Summary of Study Variables

A.	Water and Suspended Particulates	1. Weight of Suspended Particulate Material. (SPM)
		2. Organic content of SPM. (POC/PON)
		3. Particle size distribution of Suspended Particulate Material
		4. Heavy Metals (Cd, Cr, Cu, Hg Ni, Pb, As, Zn) Soluble, particulate.
		5. Petroleum-Related Hydrocarbons (Polycyclic Aromatic Hydrocarbons - PAHs, Nonpolar Hydrocarbons - Normal and Branched Alkanes) soluble, particulate.
		6. Chlorinated Hydrocarbons.
		7. Nutrients (Soluble Reactive Phosphorus, Reactive Nitrate plus Nitrite, Reactive Silicate)
B.	Supporting Data Required	1. Water Flow
		2. Water Quality Parameters (Major Ions)

approximately 100 m to each side. Sampling was at 2 depths (20% and 60% of total water depth) at mid channel and at the depth of maximum current at the other stations. Current measurements were made at ten verticals as in 1985 and a Seastar in situ sampler was moored in the East Channel for one month. Short-term time series measurements were carried out at the East Channel centre site (three samplings in an approximate 15 h period). A summary of sampling trips is given in Table 2.2.

2.1.3 Field Methods

Sampling was done through the ice in both 1985 and 1986. Access to the sites was via ice roads. The main ice road between Inuvik and Tuktoyaktuk follows the East channel downstream of Tununuk Pt. In 1985, the sampling location was chosen because of the road location and because there was some suggestion that locations further downstream might be subject to intrusion of sea water. To check this, a current meter was moored 2 m from the bottom at a location 25 km further downstream (Figure 2.1).

The four locations sampled in 1986 (Figure 2.2) were all accessible by GNWT ice roads or ice roads made to service oil company drilling rigs in the delta. At each location in both 1985 and 1986, a track was plowed across the channel to allow vehicle access.

At a central location, a portable insulated Hansen tent (8' x 16') was erected which served as a base to collect and process samples. The tent was heated with a propane furnace to reduce the risk of hydrocarbon contamination. Samples were collected from other sites across channel using a heated van for support.

Holes in the ice were made in 1985 with a gasoline driven ice auger (25 or 30 cm diameter); in 1986 a hot water ice drill was used to make larger diameter holes (46 cm) at central locations to facilitate deployment of in situ samplers. Power was provided for pumps and the continuous-flow centrifuge system by a 5 kW gasoline powered generator located about 10 m from the tent.

A summary of sampling and storage methods is given in Table 2.3 Further detail is given in the following sections.

2.1.3.1 Current Measurements

Current measurements were made with an Aanderra Instruments Recording Current Meter Model 4 (RCM-4). This meter uses a Savonius type rotor and is

Table 2.2.

Summary of Sampling Trips

Dates	Locations	Number of Verticals Sampled	Number of Verticals at Each Location for Chemical Parameters	Maximum Depth of Channel (m)	Width (m)
April 15-20, 1985	East Channel, just past Swimming Pt. at mouth of Holmes Creek	10	5	14	390
February 1-8, 1986	As above	5	3	14	480
	Main Channel just above Napoiak Channel	6	3	32	790
	Reindeer Channel	4	3	24	500
	Middle Channel	5	3	33	280

Table 2.3.

Summary of Sampling and Storage Methods

Parameter	Method of Sampling/Measurement	Storage/ Preservation
Depth	Weighted line	-
Ice Thickness	2.5 m graduated aluminum "T"	-
Current Speed	Aanderaa RCM-4 current meter direct readout; one meter moored 2 m from bottom for one week in 1985, one meter moored in East Channel for one month in 1986	data recorded internally on magnetic tape
Nutrients	PVC 3 L water bottle	Phosphate in glass; nitrate silicate in plastic/frozen
Major Ions	PVC 3 L water bottle	250 mL dilute acid (HNO_3) cleaned polybottles/ frozen
Suspended Particulates	PVC 3 L water bottle	Transferred to 1 L polyethylene bottle
	Envirodata Sedisamp System-I continuous-flow centrifuge (Ongley and Blachford, 1982) for trace metals, hydrocarbons in 1986.	Decant stored in polyethylene bottles, solids frozen in jars (trace metals) or on glass fibre filters wrapped in aluminum foil (hydrocarbons)
Particle Size	3 L PVC sampler	Transferred to 250 mL polyethylene bottles/allowed to warm to room temperature
Trace Metals	Pressure activited polyethylene sampling head as per Fletcher and Polson (1982): water collected directly into 500 mL polyethylene storage bottles. for Hg, water transferred immediately after collection into 500 mL Pyrex bottles	Some samples filtered under reduced pressure through 0.4 µm pore diameter Nuclepore filter (acid cleaned) using an all polyethylene and Teflon acid cleaned filtration assembly/frozen
	Seastar <u>in situ</u> sampler	8-hydroxyquinoline on XE-305 columns/kept cool

Table 2.3, cont'd.

Summary of Sampling and Storage Methods

Parameter	Method of Sampling/Measurement	Storage/ Preservation
Hydrocarbons	Collected directly into one gallon cleaned glass	Filtered and extracted within one day of collection or preserved storage bottles using anwith 50 mg $HgCl_2$ per 4 L and NBS type drop samplerprocessed within 10 days/water samples stored at 4°C protected from light; filters (Gelman AE) frozen in aluminum foil pouches.
	Seastar in situ sampler	XAD-2 columns/kept cool, wrapped in aluminum foil. Glass fibre filters/frozen in aluminum foil pouches.

capable of speed measurements within the range of 2.5 to 250 $cm \cdot sec^{-1}$ with an accuracy of plus or minus 1 $cm \cdot sec^{-1}$ or plus or minus 2% of actual speed, whichever is Thecurrent meter is also equipped with a 0 to 137.9 dBar pressure sensor with a resolution of 0.1% of range and an accuracy of plus or minus 1% of range.

In 1985, current measurements were made at each location (10 verticals). Measurements were made for 2 minutes at 2 m depth intervals. Data was transmitted directly to the surface and printed out with an Applied Microsystems Digiprint. At station 5, current profiles were taken at the beginning of sampling and again 3 days later. Another meter was moored 2 m from the bottom (water depth 14 m) at a site about 25 km downstream for a one week period (Figure 2.1). This was done to determine whether there were any intrusions of salt water from Kugmallit Bay.

In 1986, current measurements were made in each channel at 2 m depth intervals as in 1985. Measurements were taken at 6 verticals in the Main Channel, 5 verticals in the East and Middle Channels and at 4 verticals in Reindeer Channel. Estimates were made in both 1985 and 1986 of the channel width (water under the ice) and water depth. A current meter was moored in the East Channel with the in situ samplers for a one month period (from February 8 - March 8). However no data was obtained due to an electrical fault in the magnetic tape drive.

In both 1985 and 1986, current measurements were made at each site from one to two weeks after sampling by Inland Waters Directorate personnel from Inuvik to accurately determine discharge.

2.1.3.2 Water

Discrete water samples were collected for suspended particulate, major ion and nutrient measurements with a 3 L capacity Niskin type PVC water sampler on a weighted polypropylene line. Water was transferred to 1 litre capacity polyethylene bottles for filtration and total suspended solid determination. Water for hydrocarbon analyses was collected with a stainless steel and Teflon to NBS type drop sampler (Green, 1979). Trace metal samples were collected with an all polyethylene and Teflon pressurized sampler (Fletcher and Polson, 1982). In both the NBS and Fletcher samplers, water is collected directly into the storage bottles. For mercury samples, water was transferred immediately after collection to 500 mL Pyrex ground glass stoppered bottles.

a) Special Cleaning Procedures for Storage/Collection Bottles:

	Bottle Type	Cleaning Procedure
Hydrocarbons	glass	solvent cleaned; then baked at 350°C overnight; sealed with cleaned Teflon cap liners. (See Section 2.2.5.1(f).)
Trace Metals (except Hg)	500 mL polyethylene	successive 3 day soaks in: 1) 4 N HNO_3 at 50°C; 2) 0.1% HNO_3 at 50°C; 3) 0.1% HNO_3 (ultra pure) at room temperature. Between soaks, bottles are rinsed with Milli-Q water. After final cleaning, bottles are triple wrapped in polyethylene bags.
Mercury	500 mL Pyrex	bottles are filled with tap water and 14 mL high purity HNO_3/H_2SO_4 (1:2) and heated at 80°C for 3 h; the procedure is repeated twice, bottles are rinsed and double wrapped in polyethylene bags.

b) Special Procedures in Sampling:

To reduce the risk of contamination, trace metal and hydrocarbon sampling gear was kept wrapped in plastic or aluminum foil (hydrocarbon sampling gear) when not in use. Trace metal sample bottles and samplers were handled with polyethylene gloved hands. After collection, trace metal samples were double wrapped in polyethylene bags.

2.1.3.3 Particulates (Metals and Hydrocarbons)

Suspended particulates in 1985 sampling were collected by filtration. Particulates for trace metal analysis were collected with the Seastar in situ sampler onto 142 mm diameter, 0.4 µm pore size Nuclepore polycarbonate membrane filters. The filters had been cleaned by successive 3 day soakings in warm 6 N HCl; 0.1% HNO_3 (Seastar) followed by copious rinses; with Milli-Q water to remove traces of acid. Filters were handled with Teflon forceps and folded after use and stored frozen in plastic petri dishes.

Particulates for hydrocarbon measurements were collected onto 142 mm glass fibre filters (Gelman AE) and stored frozen (see Section 2.2.5.2a).

In 1986, particulates were collected as in 1985 by filtration. In addition, a continuous-flow centrifuge system, the Sedisamp System-I (Envirodata, Ongley and Blachford, 1982) was used to collect large quantities of particulates. One sample was collected from each channel at a centre location (5 - 8 m). Water from a Little Giant submersible pump was delivered at 6 L min^{-1} to a stainless steel ball valve splitter and supplied to the centrifuge at a rate of 4 L·min^{-1} using cleaned 1/2" I.D. polyethylene tubing. The centrifuge was operated inside the Hansen tent.

Suspended sediment from the centrifuge was recovered by decanting excess water into cleaned polyethylene bottles. Half of the residual bowl sediment was scraped off with a spatula swabbing with cleaned glass fibre filter pads for hydrocarbon analysis. The collected residues were placed on a glass fibre filter and wrapped in cleaned aluminum foil and stored frozen. The remaining sediment was scraped from the centrifuge bowl with a Teflon spatula and placed in a glass jar for trace metal analyses. Decant water was later filtered in the lab through tared 0.4 µm Nuclepore filters to obtain a measure of total sediment. Subsamples of the Reindeer Channel and Main Channel organic sample were weighed out for independent intercalibration analysis at another lab. The East Channel organic samples were subsampled for particle size analysis by Sedigraph and the remaining sample split for hydrocarbon and chlorinated hydrocarbon analysis. Details of the sample sizes and use of material collected are given in Table 2.4.

Particulate loads calculated on the basis of a discrete sample and subsequent filtration give results for an instantaneous point in space and time. Both the Seastar sampler and Sedisamp give time-integrated samples over many hours.

2.1.3.4 Seastar In Situ Sampler

The Seastar samplers were deployed in both 1985 and 1986 sampling periods. In 1985, repetitive samples were collected at the centre location (No. 5); the sampler was deployed from within the heated tent and allowed to pump for periods of 4 to 18 hours.

In 1986, in situ samples were collected at the centre location in all channels. In addition, 2 samplers, one for metals and one for hydrocarbons, were left at the East Channel east site for a one month period and recovered in early March.

Table 2.4.

Continuous-Flow Centrifuge Sediment, Subsampling Sizes and Division of Samples

Channel	Sample Id.	Vol. (L)	Total[a]	Dry Wt. of Subsample (g) Inorganic	Organic	Other
Middle	SS-2-1	1482	1.62	0.998	0.626	-
Reindeer[b]	SS-2-2	1452	2.49	1.955	0.233	0.305 inter-calibration
Main[c]	SS-2-3	1516	2.89	2.158	0.344	0.389 inter-calibration
East[d]	SS-2-4	4260	7.19	3.736	1.012	0.836 chlorinated HC's. 1.608 particle size analysis

a Total calculated from decant residue + (inorganic sediment x 100/x)

where: x = % of sediment taken for inorganic analysis
(2,3,4 = 50%; 1 = 40%)

b 43% of organic sample retained and used for hydrocarbon analysis.

c 47% of organic sample retained and used for hydrocarbon analysis.

d 29% of organic sample retained and used for hydrocarbon analysis;
24% used for chlorinated hydrocarbon analysis;
47% used for particle size analysis.

For trace metals, 8-hydroxyquinoline bonded to XE-305 resin columns (Seastar Instruments Ltd.) were used. Cleaned (see Section 2.1.3.3) 142 mm 0.4 µm pore diameter polycarbonate Nuclepore filters were used in the filter housing. For hydrocarbon sampling, columns with an XAD-2 resin were used with baked Gelman AE glass fibre filters (nominal pore size 1.0 µm). A summary of deployments and volumes processed for trace metals and hydrocarbons is given in Table 2.5.

Before and after field use, the flow rate and volume calibration accuracy was determined for each sampler. After the 1986 field program, a minor change in the calibration accuracy was reported by Seastar for the instruments, but this was within ±2% of the specification after six weeks in the field.

2.2 Analytical Methods

2.2.1 Suspended Particulate Material (SPM)

2.2.1.1 Weight

Sub-samples were drawn from 3 L PVC samplers immediately after recovery into twice rinsed 1 litre polyethylene bottles. Samples were stored unfrozen until return to the laboratory in Inuvik where the contents were filtered under reduced pressure through tared 47 mm, 0.4 µm pore diameter Nuclepore filters. The volume filtered was measured after filtration by pouring the filtrate into a graduated cylinder. Filters were stored in plastic petri dishes until returned to Sidney. Samples were oven dried at 60°C to constant weight, then reweighed on an analytical balance to the nearest 0.01 mg. Accuracy of the weighing was estimated using Class P weights (traceable to NBS tolerances) to be ± 0.02 mg. Repeatability as determined by filtration and weighing of 5 replicate aliquots from the same PVC sampler was 6.3% (relative standard deviation).

2.2.1.2 Particle Size

Particle size of suspended particulate material was measured by three separate techniques:

1) Coulter Electronics Model TA II particle counter of river water samples;

Table 2.5.

Summary of Seastar In Situ Sampler Deployments

Date	Type of Column	Channel	Mode[a]	Flow ($mL \cdot min^{-1}$)	Pumping Time (h)	Volume (L)	Comments
18/04/85	XE305	East	C	200	2.0	24.03	
18/04/85 - 19/04/85	XE305	East	-	200	1.8	22.01	left in overnight: 18 h, pumped for 6 min. each hour
19/04/85	XE305	East	C	100	2.8	16.56	
20/04/85	XE305	East	C	200	3.0	36.24	
18/04/85	XAD-2	East	C	200	8.3	100 (?)	flow meter not working
19/04/85	XAD-2	East	C	200	1.0	12.20	
20/04/85	XAD-2	East	C	200	4.7	54.34	
31/01/86	XAD-2	Middle	C	100	13.0	81.61	
01/02/86	XAD-2	Middle	C	100	6.9	41.37	
3/02/86	XAD-2	Reindeer	C	100	6.3	37.54	
4/02/86	XAD-2	Reindeer	C	100	12.0	69.01	
4/02/86	XAD-2	Main	C	100	3.6	22.18	
5/02/86	XAD-2	Main	C	100	6.0	0.17	failed to work
7/02/86	XAD-2	East	C	100	10.5	63.08	
7/02/86	XAD-2	East	C	150	8.0	70.86	
8/02/86 - 11/03/86	XAD-2	East		100	-	99.26	pumped for 35 min. each 12 h for 28 days
01/02/86	XE305	Middle	C	100	6.6	40 (?)	flow meter not operative
03/02/86	XE305	Reindeer	C	100	5.8	33.71	no filter used
5/02/86	XE305	Main	C	100	6.0	37.86	
7/02/86	XE305	East	C	100	7.0	42.68	
8/02/86 - 11/03/86	XE305	East	-	100	-	38.71	pumped for 16 min. each 12 hours for 28 days

a) C = continuous pumping

2) HIAC/ROYCO model 346B forward light scattering counter of river water samples; and

3) A Micrometrics Sedigraph 5000D analysis of of bulk dried sample collected with a Sedisamp System-I continuous-flow centrifuge.

Each method is based on different physical principles and measures different properties. The Coulter Counter is based on changes in electrical resistivity as particles pass through a small orifice and gives a measure of particle volume. The HIAC/ROYCO analyzer measures the amount of low-angle, forward-scattered light refracted by particles as they pass through a laser beam. The Sedigraph measures settling velocity of particles in a liquid with x-ray sensors. The HIAC/ROYCO requires no sample pretreatment. Electrolyte must be added for Coulter Counter analysis. The Sedigraph requires a relatively large amount of solid material (0.5 g) which is pre-treated before analysis.

a) Coulter Counter:

A Coulter Counter Model TA II was used in April 1985 sampling using a 100 µm aperture tube. To increase and normalize ionic strength, samples were treated with concentrated, particle free sodium chloride solution (obtained by filtering through 0.4 µm Nuclepore filters). Samples ready for analysis were 4% in NaCl. Total particle count and percent of total volume in a given size range were measured at a steady flow rate for a period of 200 seconds. The calibration of the instrument was verified every day by analysing standard solutions. Particle free electrolyte (4% NaCl) was analyzed to establish background contribution.

It was planned to analyze samples in the field immediately after collection. Power surges from the generator made field measurements impractical after the initial few samples had been analyzed. Subsequently some samples were returned to Inuvik and analyzed 24-48 h after collection. To determine the effect of long-term storage both with and without added electrolyte, a study was carried out using water from a local stream in Sidney, B.C. Results are summarized in Table 2.6. There appears to be little change in distribution of particles in samples stored for up to 72 hours. Some samples from 1986 sampling were also analyzed by Coulter Counter approximately 4 weeks after collection in Sidney, B.C. for comparative purposes with the HIAC/ROYCO results.

Table 2.6.

Coulter Counter Particle Size Analysis - Storage Study

Fresh Water Samples	Storage Time (h)	% Total Volume in Size Range (μm) 1.26-1.59	1.59-2.00	2.00-2.52	2.52-3.17	3.17-4.00	4.00-5.04	5.04-6.35	6.35-8.00	8.00-10.08	10.08-12.7	12.7-16.0	16.0-20.2	20.2-25.4	25.4-32.0	32.0-40.3
Storage Condition:																
Sample stored in 10 L. jug. Electrolyte (NaCl) added 15 min. before analysis	0.3	5.4	5.4	6.3	4.6	6.3	9.3	8.3	5.2	4.5	10.6	6.0	5.7	14.8	4.0	3.9
	2.0	5.6	5.9	7.1	5.0	7.1	9.4	8.0	5.1	4.3	9.8	7.7	5.5	10.2	3.1	6.8
	3.0	4.9	5.2	6.0	4.4	6.1	8.2	6.8	4.2	14.7	8.9	7.9	7.2	11.7	2.8	11.2
Test:	4.0	5.3	5.5	6.5	4.6	6.3	8.3	7.2	4.9	4.6	9.6	7.3	6.3	12.0	4.2	7.6
Changes in particle distribution on storage of untreated sample.	7.0	5.1	5.4	6.1	4.3	6.3	8.0	6.7	5.1	4.9	8.1	5.6	5.5	11.8	4.1	13.0
	24.0	7.2	8.4	8.4	5.2	6.7	7.7	6.7	5.0	4.9	8.2	5.7	6.1	11.9	3.9	4.3
	72.0	4.0	5.5	7.5	6.8	8.7	9.7	11.0	6.8	5.3	7.4	6.3	5.0	7.9	3.3	4.8
Storage Condition:																
Sample stored in 10 L jug. Electrolyte (NaCl) added shortly after sample collection.	0.50	4.9	5.2	6.0	4.4	6.1	8.2	6.8	14.7	4.2	8.9	7.9	7.2	11.7	2.8	11.2
	0.75	5.4	5.6	6.7	4.8	6.8	9.1	7.4	4.8	4.9	7.3	8.7	8.1	13.2	3.8	3.4
Test:	1.00	5.5	5.7	6.9	4.9	7.0	9.3	7.3	4.8	4.9	8.4	8.8	8.0	12.2	3.9	2.9
Changes in particle size distribution on storage of NaCl treated samples.	24.00	6.9	5.3	4.4	3.0	4.6	6.7	6.3	5.3	5.5	8.6	8.9	10.8	15.0	4.7	4.3
	72.00	4.1	2.5	2.2	2.1	3.4	5.2	7.6	7.3	6.9	11.7	9.0	14.6	11.2	4.6	8.0

b) Light Scattering:

A HIAC/ROYCO model 346B counter was used to measure particle size from 1986 samples. Two sensors were used: 346 BCL which allows measurements from 0.4-16 µm and CMH 150 which allows measurements in the range 3.1-124 µm. Measurements were made as per the manufactuers' instructions. Measurements in Inuvik, January 1986 could only be done with the CMH 150 sensor due to problems with the 346 BCL. The instrument was calibrated with solutions of latex spheres with a size distribution of 5.0, 10.0 and 20.0 µm. For the 5.0 µm standards, the peak in particle counts was at 3.9 µm (Appendix B). Samples were analyzed within 12 h of collection, in Inuvik. Analysis was done on approximately 10 mL sample aliquots at a flow rate of 0.8 $mL \cdot sec^{-1}$ to give a total of 10,000 counts. Background levels were typically <100 counts in 10 mL. Samples were collected in cleaned (ultrasonic) polyethylene bottles, and stored unfrozen. Samples were returned to Sidney and samples from each channel sent to L. Miller Associates, California for analysis using a 346 BCL sensor. These analyses were undertaken 3-4 weeks after the samples had been collected.

c) Sedigraph Analysis of Bulk Sample:

A portion (approx. 1 g dry weight) of the sample from the Main Channel site collected by the Sedisamp System-I used for obtaining suspended particulates for hydrocarbon and trace metal analysis, was analyzed by Sedigraph. The analysis was done at the Pacific Geoscience Centre, Sidney, B.C. The sample was freeze dried and then resuspended in 50 mL of a 0.5% sodium hexametaphosphate solution to prevent flocculation. The solution was placed in an ultrasonic bath for 30 minutes before Sedigraph analysis.

2.2.1.3 Particulate Organic Carbon and Nitrogen

Particulate organic carbon and nitrogen were determined with a Perkin-Elmer 240 Elemental Analyser using standard operating conditions by K. Iseki at the Institute of Ocean Sciences, Ocean Chemistry Division, Sidney, B.C. Inorganic carbonates were eliminated from the filters by exposure to hydrochloric acid vapour for 8 h in a closed container. Samples were pyrolysed at 800°C in a quartz boat and the instrument was calibrated daily with acetanilide. Instrumental precision was 0.12% carbon and 0.12% nitrogen.

2.2.2 Major Ions

Separate water samples were collected from 3L PVC samplers for analysis of major cations (Al^{3+}, Mg^{2+}, Na^{+}, Ba^{2+}, K^{+}, Fe^{3+}, Ca^{2+}) and anions (Cl^{-}, F^{-}, SO_4^{2-}). Samples for cations were stored in acid cleaned (4 N HNO_3 - "Instra Analyzed Grade" for 4 days) 250 mL polyethylene bottles. Samples for anion analysis were stored separately in 125 mL polyethylene bottles (cleaned with a dilute (1%) nitric acid soak for 1 day followed by rinses with Milli-Q water). Samples were analyzed under subcontract by Quanta Trace Laboratories Ltd. in Vancouver. Samples for cations were analyzed directly by inductively coupled argon plasma spectrometry (ICP). A Spectrometrics model 3B ICP was used with a modified high pressure cross flow nebulizer. The spectrometer is directly coupled to a PDP 11-23 minicomputer. Anions were analyzed directly with a Dionex model 12S ion chromatograph. Samples of reference materials were submitted for analysis for cations and samples were analyzed by the laboratory as part of its own quality control program. Results are given in Table 2.7. Precision (including sampling, storage and analysis) was estimated on the basis of analysis of triplicate samples from East Channel, 1985, and is summarized in Table 2.7.

Concentrations of Al in 1985 samples were about 7.5 $mmol \cdot m^{-3}$ for unfiltered samples and about 5.4 $mmol \cdot m^{-3}$ for filtered samples. Analyses of the SLRS-1 riverine reference material which became available in summer 1986 however, indicated a blank or calibration problem. Aluminum values were 8 times higher than the certified level. Samples from 1986 run at the same time gave results in agreement with 1985 data. After the problem was identified and corrected, Al concentrations in filtered samples were 1.1 to 2.2 $mmol \cdot m^{-3}$; unfiltered levels were also lower. It would appear therefore that the 1985 aluminum data is in error.

2.2.3 Nutrients (Reactive Silicate, Orthophosphate, Nitrate)

Samples for nutrient analysis were collected in duplicate from 3 L PVC samplers and drawn into twice rinsed polyethylene (silicate) and Pyrex glass (phosphate, nitrate) vials (10 mL). Samples were stored frozen until analyses. Care was taken to freeze samples slowly to prevent breakage of the tubes.

Analysis was by standard colorimetric techniques (as outlined by Macdonald and McLaughlin (1982)) using a Technicon II Autoanalyzer. Samples were unfiltered. Plastic vials were allowed to thaw for 24 h before analysis for silicate.

Table 2.7.

Accuracy and Precision of Major Ion Analyses (all values in $mg \cdot L^{-1}$)

Metal/Anion	EPA TM-1-1 & TM-1-2 WP-284			EPA Min-2 Mineral QC		SLRS-1 Riverine Reference Material (values in $\mu g \cdot L^{-1}$)		Precision[a] %
	True	Mean Recovery	Found (n=9, TM-1-1) (n=12, TM-1-2)	Certified	Found (n=9)	Certified	Found (n=3)	
Al	0.107 0.729	0.135 ± 0.023 0.745 ± 0.063	0.17 ± 0.08 (3) 0.75 ± 0.06 (3)			23.5 ± 1.2	30 ± 10 (3)	5.1
Ca				5.3 ± 0.4	5.43 ± 0.19 (3)	25.1 ± 0.9	30.1 ± 0.3 (3)	2.1
Ba						22.2 ± 1.7	19.3 ± 0.6 (3)	2.3
Mg				1.8 ± 0.2	1.89 ± 0.11 (3)	5.99 ± 0.28	5.82 ± 0.02 (3)	15.8
K				2.1 ± 0.2	2.2 ± 0.2 (3)	1.3 ± 0.2	1.2 ± 0.1 (3)	14.8
Na				8.2 ± 0.5	9.00 ± 1.16 (3)	10.4 ± 0.6	9.2 ± 0.1 (3)	10.6
Fe	0.0209 0.797	0.022 ± 0.005 0.789 ± 0.046	0.02 ± 0.005 (3) 0.792 ± 0.014 (3)			31.5 ± 2.1	>100	4.5
Mn						1.77 ± 0.23	< 1	1.0
Cl				17.8 ± 0.95	19.2			16.3
F				0.43 ± 0.03	0.42			31.5
SO_4				7.2 ± 1.18	7.0			1.0

a - based on relative standard deviation of triplicate samples in April, 1985 worst case (includes sampling, storage and analytical variability).

Note: uncertainty expressed as ±1 standard deviation except for SLRS-1, where uncertainty of certified value is 95% tolerance limits.

Nitrate refers to the amount of reactive nitrate plus nitrite ions; silicate to the amount of soluble reactive silicate; and phosphate to the concentration of soluble reactive inorganic orthophosphate ions (SRP). The technique for silicate analysis involves formation of beta-molybdosilicic acid in acid medium which is subsequently reduced by ascorbic acid to form the characteristic molybdenum blue colour. Oxalic acid is used to prevent interference from phosphate. Nitrate is analyzed by reduction to nitrite in a copper-cadmium reductor column. The nitrite reacts with sulfanilamide in acid to form a diazo compound which on coupling with N-(1-naphthyl)ethylenediamine dihydrochloride forms a red azo dye. Orthophosphate is determined by forming molybdophosphoric acid which is reduced by ascorbic acid to give the molybdenum blue colour. In all three cases absorbance of the coloured complex is measured. Samples were not filtered and the absorbance was uncorrected for turbidity.

The precision of the analytical methods was ± 0.3% for silicate and phosphate and ± 0.4% for nitrate. The accuracy based on the use of Sagami standards was ± 5% for silicate and phosphate and ± 4% for nitrate (±2 sigma limits).

2.2.4 Trace Metals

2.2.4.1 Particulates

a) Preparation

April 1985 samples were collected on filters (0.4 µm Nuclepore) using the *in situ* sampler. In the laboratory, particulates were removed from dried filters for analysis as follows:

1) filters were crumpled and the particulates collected on a clean Teflon sheet.

2) the particulates were scooped up with a Teflon coated spatula into a tared plastic petri dish, dried for 1 h at 40°C, then weighed.

3) the dried material was divided into 3 aliquots of ~20 mg each for bomb digestion.

February 1986 samples from the continuous-flow centrifuge system were dried at 40°C for 24 h, in plastic dishes (polypropylene) then pulverized in an agate mortar to a fine powder.

b) Copper, Cadmium, Lead, Zinc, Nickel, Vanadium, Chromium and Arsenic

Digest:

Dried samples were digested in sealed Teflon bombs with a mixture of aqua regia and hydrofluoric acid using a modification of the procedure of Buckley and Cranston (1971): an approximate 10 - 80 mg (larger size for Sedisamp particulates) sample was transferred to a Teflon bomb and wetted with 0.2 mL aqua regia (1:3 v/v HNO_3:HCl, Baker, 'Instra Analyzed') and 1 mL of HF (Seastar). The bomb was sealed and heated on a hot plate at 100°C for 1 h. After cooling to room temperature, the contents of each bomb were transferred to a tared 30 mL polyethylene bottle containing 3 mL of 4% boric acid solution (BDH, assured). The bomb was rinsed with Milli-Q water, the rinse water added to the polybottle and the total weight brought to 25 g.

Analyses:

All metals were measured in the final digest by graphite furnace atomic absorption. Standardization was from a standard curve with the matrix matched to that of the digest (same concentrations of acids, boric acid plus silicon, iron and aluminum based on assumed concentration of 60%, 5% and 16% Si, Fe and Al respectively in the sediment). Arsenic was analyzed using a Tantalum coated tube to reduce interferences before analysis. Samples were diluted 1:1 with a 1000 $mg \cdot L^{-1}$ Ni solution.

A Perkin Elmer model 703 AA equipped with an HGA 500 furnace, AS-1 autosampler and deuterium arc background correction was used for analyses. Pyrolytically coated graphite tubes were used for all metals.

Precision and Accuracy:

Samples (50 mg) of standard marine reference materials (MESS-1 and BCSS-1, National Research Council) were carried through the procedure to

assess accuracy and precision. Results of these analyses are given in Table 2.8 along with blanks and detection limits. Results for Pb are low. Recoveries are about 60% of certified levels, possibly as a result of matrix effects in atomization. Results for other metals, despite the small sample size, were within the 95% tolerance limits except for As and V with BCSS-1. In both cases BCSS-1 results were high by about 10-20%. Results are reported uncorrected.

c) Mercury

Digest:

Dried samples were digested in Pyrex bottles with hot nitric:sulphuric acid after the procedure by Hatch and Ott (1968). An approximate 10-80 mg sample was transferred to a cleaned 500 mL Pyrex bottle to which were added 7 mL of a 1:2 mixture of HNO_3:H_2SO_4 (both Baker "suitable for mercury analysis" grade). The bottles were placed in a water bath at 80°C for 3 h, allowed to cool to room temperature, then diluted with 250 mL of tap water.

Analysis:

The mercury in the sediment was oxidized with 7 mL of 80% HNO_3:20% H_2SO_4(v/v) at 80°C for 3 h. Bottle and acid blanks were prepared in the same way.

After cooling to room temperature, the water samples with 500 mL were divided into two 250 mL aliquots. The mercury was reduced to elemental mercury by adding 3 mL of a 20% (w/v) stannous chloride solution and swirling for 30 seconds. After standing for a further 30 seconds, the mercury was driven off in a stream of dry nitrogen gas(flow rate 0.4 $L \cdot min^{-1}$) into a 30 cm path length cell of a Laboratory Data Control UV monitor. The mercury peak absorbance at 257.9 nm is proportional to its concentration. The instrument was calibrated at the beginning and end of each run or after 6 samples. Calibration was carried out by adding mercuric ion (2 ng or less) to approximately 250 mL of tap water. The mercury was

Table 2.8

Performance Characteristics of Trace Metal Analyses in Particulates
(units μmol.kg-1; mmol.kg-1 for Cr, Zn and V)

Element	MESS-1 certified[1]	MESS-1 found[2]	BCSS-1 certified[1]	BCSS-1 found[2]	Blank (μg)	Detection Limit[3] (μg)	Detection Limit[3] (μmol.kg^{-1})
Arsenic	142 ± 16	139 ± 7 (3)	148 ± 19	203 ± 29 (4)	<0.2* -		< (80)
Cadmium	5.25 ± 0.89	5.16 ± 0.71 (4)	2.23 ± 0.36	2.05 ± 0.27 (3)	0.001 ± 0.001 (6)	0.003	(1.34)
Copper	395 ± 60	425 ± 94 (6)	291 ± 42	308 ± 46 (6)	0.08 ± 0.03 (6)	0.09	(71)
Chromium	1.37 ± 0.21	1.25 ± 0.17 (5)	2.37 ± 0.27	2.23 ± 0.12 (5)	0.15 ± 0.08 (6)	0.24	(0.23)
Lead	164 ± 29	117 ± 14 (4)	110 ± 16	80 ± 19 (4)	<0.05*		< (14)
Nickel	502 ± 46	477 ± 58 (6)	942 ± 61	891 ± 34 (6)	<0.2*		<(170)
Vanadium	1.42 ± 0.1	1.56 ± 0.14 (4)	1.83 ± 0.10	2.26 ± 0.19 (4)	<0.9*		< (0.9)
Zinc	2.92 ± 0.26	3.09 ± 0.31 (6)	1.82 ± 0.18	1.90 ± 0.15 (4)	0.3 ± 0.1 (6)	0.3	(0.23)
Mercury	0.853 ± 0.070	0.828 ± 0.050 (6)	0.643 ± 0.060	0.654 ± 0.050 (3)	0.002 ± 0.005 (6)	0.0015	0.300

* Blank below detection.
1. Values are ±95% tolerance limits.
2. Values are ±1 standard deviation (n in brackets).
3. Defined as 3 x standard deviation of the blank. Value in brackets calculated for 20 mg of sample.

The values given indicate a problem for Pb (values are low by about 40%) possibly due to matrix effects.

reduced to elemental mercury with the addition of stannous chloride as in the regular procedure. Three such spiked samples were run at the beginning and end of a batch of samples (6 or less). A blank corresponding to tap water and stannous chloride/sulphuric acid was run in triplicate and the mean subtracted from the mean of the spiked samples. A linear response was assumed. Reagents used were all Baker-Analyzed, 'suitable for mercury analysis' grade. Sodium dichromate was Baker-Analyzed Primary Standard grade. The solution containing 20% (w/v) stannous chloride and 20% (v/w) sulphuric acid was prepared in tap water and purged with nitrogen for 4-6 hours to remove traces of mercury.

Precision and Accuracy:

Analyses of 50 mg aliquots of MESS-1 and BCSS-1, marine reference sediments (NRC, Ottawa), were performed. For both sediments, mercury concentrations were within the 95% tolerance limits of the certified values (Table 2.8).

2.2.4.2 Trace Metals in Water

a) Preparation

Water samples were collected directly into 500 mL cleaned (see Section 2.1.3.2) polyethylene bottles. Samples for mercury analysis were collected in polyethylene bottles and immediately transferred to 500 mL Pyrex ground glass stoppered bottles. Bottles were stored wrapped in polyethylene until returned to the laboratory in Sidney, B.C. Some samples were then filtered. Sample manipulations and filtrations were carried out in a clean room providing class 30 -100 working areas. Filtration of samples was under reduced pressure through cleaned Nuclepore 0.4 µm 47 mm diameter membrane filters. Filters were cleaned by a warm (45 -50°C HNO_3 (Seastar Chemical Ultrapure) in Milli-Q water) soak for 6 h followed by rinses with Milli-Q water and a 0.1% HNO_3 soak for 2 days. The filter and filter holder, and all tubing were of Teflon and conventional polyethylene which had been cleaned as per storage bottles (Section 2.1.3.2). All samples in polyethylene bottles (after filtration) were acidified with 1.0 mL nitric acid, then heated at 50°C in a water bath for 24 h to liberate any metals absorbed onto the bottle walls.

Results are therefore for dissolved plus readily acid-leachable particulate metal from bottle walls for Cu, Cd, Pb, Zn, Cr, Ni and As in filtered samples. A measure of the total metal available from particulates can be obtained from the metal data for particulates and the concentration of SPM. In most cases the particulate metal, even if 100% were liberated by acidification, would account for a small percentage of the dissolved plus acid leachable concentrations. Mercury samples were subjected to a total digest in the bottle and therefore give a measure of "total" concentrations. Dissolved levels can be estimated by subtracting the particulate fraction based on mean SPM concentrations and concentrations of mercury in particulates.

b) Copper, Cadmium, Lead, Nickel, Zinc, Chromium and Vanadium

Copper, nickel, vanadium and zinc were determined directly by graphite furnace atomic absorption. It was necessary, however, to preconcentrate samples for Cd, Pb and Cr analyses.

Samples were preconcentrated by evaporation of 100 mL of sample to approximately 10-15 mL in quartz beakers under a class 10 clean hood at 50°C. Metals were determined in the concentrated samples by graphite furnace atomic absorption spectrometry. Samples were delivered to the HGA 500 furnace with an AS-1 auto sampler mounted in a Perkin Elmer model 703 atomic absorption (AA) spectrometer. Conditions were standard conditions recommended for each element by the manufacturer with lower gas flows during atomization to increase sensitivity when necessary. Cadmium, lead and zinc analyses were run with deuterium arc background correction. Standardization was via a working curve prepared by running a mixed standard (all elements) in 0.2% HNO_3 (or 2% for concentrated samples) for Cu, V and Cr. For the other metals, the method of standard additions was used. This was found to be necessary due to the influence of matrix effects on sensitivity.

c) Mercury

In 1985, all samples were split. Half (~250 mL) of the sample was filtered through baked (450°C for 6 h) GFC filters. Filtrates were stored in mercury cleaned 500 mL Pyrex bottles. In 1986, samples were not filtered.

The mercury in the filtered and unfiltered samples was oxidized with 7 mL of 80% HNO_3:20% H_2SO_4(v/v) at 80°C for 3 h. Bottle and acid blanks were prepared in the same way.

After cooling to room temperature, the water samples with 500 mL were divided into two 250 mL aliquots. The mercury was reduced to elemental mercury by adding 3 mL of a 20% (w/v) stannous chloride solution and swirling for 30 seconds. After standing for a further 30 seconds, the mercury was driven off in a stream of dry nitrogen gas (flow rate 0.4 $L \cdot min^{-1}$) into a 30 cm path length cell of a Laboratory Data Control UV monitor. The mercury peak absorbance at 257.9 nm is proportional to its concentration. The instrument was calibrated at the beginning and end of each run or after 6 samples. Calibration was carried out by adding mercuric ion (2 ng or less) to approximately 250 mL of tap water. The mercury was reduced to elemental mercury with the addition of stannous chloride as in the regular procedure. Three such spiked samples were run at the beginning and end of a batch of samples (6 or less). A blank corresponding to tap water and stannous chloride/sulphuric acid was run in triplicate and the mean subtracted from the mean of the spiked samples. A linear response was assumed. Reagents used were all Baker-Analyzed, 'suitable for mercury analysis' grade. Sodium dichromate was Baker-Analyzed Primary Standard grade. The solution containing 20% (w/v) stannous chloride and 20% (v/w) sulphuric acid was prepared in tap water and purged with nitrogen for 4-6 h to remove traces of mercury.

d) Arsenic

In 1985, samples were analyzed by Quanta Trace Laboratories Ltd. in Vancouver. All 1986 samples were analyzed by Arctic Laboratories.

The methods used were:

1985 samples:

140 mL of sample was placed in an acid washed 300 mL tall form Pyrex beaker and evaporated on a hot plate to approximately 7 mL. The remaining sample was transferred with 20 $mohm \cdot cm^{-1}$ water (DI water) to 15 mL polycarbonate tubes and the volume adjusted to 14.0 mL with DI water. The arsenic in the concentrated samples was reduced with sodium borohydride and the arsenic generated swept by argon into the argon plasma of a Spectrometrics model 3B ICP. The resulting emission is measured at 193.67 nm.

Blanks of DI water were carried through the procedure and values found to be $<1.3\ \mu mol \cdot L^{-1}$. Analysis of NBS 1643a water gave an As concentration of $1.04\ mmol \cdot L^{-1}$. The certified level was $1.03 \pm .009\ mmol \cdot L^{-1}$.

1986 Samples:

Arsenic was determined using a hydride generation technique after Andreae (1977). Samples (100 mL) were combined with 10 mL of 6 M hydrochloric acid in the reaction vessel and purged with helium for 4 minutes. At the concentration of acid (0.54 M) it has been reported (Agemian and Thompson, 1980) that both arsenic III and arsenic V are detected with the same sensitivity. The sample trap (U-tube) was placed in a liquid nitrogen bath and allowed to cool for at least two minutes. Sodium borohydride solution (6 mL of 4% w/v) was added at a rate of 3 $mL \cdot min^{-1}$ using a 10 mL plastic syringe with a Teflon extension tube. The sample solution was stripped for 6 minutes, including the 2 minutes to add the borohydride, then the trap was removed from the liquid nitrogen and allowed to warm to room temperature. The volatilized arsine was swept by helium gas into the hot (800°C) quartz furnace, positioned in the light path of a Perkin Elmer 2380 spectrophotometer. At a helium flow rate of 60 $mL \cdot min^{-1}$, the arsenic signal appeared after about 17 seconds. Peak area was recorded using the appropriate mode on the PE 2380. Integration was initiated 15 seconds after warming the trap and continued over 40 seconds.

Arsenic values were determined by interpolation from a least squares calibration curve using standards run before and after each set of samples.

Operating conditions are summarized below.

PE 2380 AAS	Wavelength 193.7 nm (193.6 nm non-calibrated wavelength selector).	
Slit	2.0 nm	
Lamp Current	10 mA	
Gain	75	
Recorder	10 mV 20 $cm \cdot h^{-1}$	
Quartz Furnace	Variac setting 24 (approx. 29 V a.c.) (estimated temperature 800°C)	
Gas Flow Rates	Helium HP:	60 $mL \cdot min^{-1}$
	Hydrogen:	90 $mL \cdot min^{-1}$
	Air:	90 $mL \cdot min^{-1}$

e) In Situ Sampler Columns

XE-305/8-hydroxyquinoline columns were eluted in the laboratory using a mixture of 1.0 M HCl:0.1 M HNO_3. The columns were eluted with 100 mL of the above mixture by filling the column and allowing the acid to sit in the column for 1 h before draining. The eluate was collected in polyethylene bottles and analyzed for trace metals. Concentrations were high enough that flame AA analysis could be carried out for Zn while flameless AA was used to measure Cd, Pb, Cu and Ni.

f) Trace Metals in Water - Precision and Accuracy

Blank levels for all elements from acid used for acidification and from storage bottles were below detection. Definition of limits of detection defined on the basis of the standard deviation of the blank was therefore not possible. A maximum limit for the analytical blank was estimated by the error in the absorbance vs concentration intercept or 0.002 absorbance units (whichever was higher). The limit of detection was defined as 3 times this value and is summarized for each metal in Table 2.9.

Accuracy was assessed by analysis of a reference riverine water, SLRS-1 (National Research Council, Canada). The water is from the St. Lawrence River and has been certified for a number of metals. Results are given in Table 2.9. Values obtained for Cu, Zn, Pb and Cr are within the 95% tolerance limits of certified values. Recoveries were low for As possibly due to incomplete hydride formation. Cadmium concentrations were about 30% too high. Vanadium was a factor of 3 too high although the uncertainty at the level of SLRS-1 water was high as the concentration was near the detection limit.

In 1985, accuracy was assessed by analysis of NBS 1643a water as SLRS-1 water was not available. Most metals were in agreement with certified levels. However, Ni, Pb, V and Zn results were all slightly high. All values have been reported uncorrected for any variations from reference material certified levels. Analytical precision as defined by the relative standard deviation was estimated by replicate analysis of SLRS-1 water. Results are summarized in Table 2.9.

The combined analytical and sampling variance was estimated by analysis of triplicate samples from various locations in 1986 and 1985. A summary of these data is given in Table 2.10.

Table 2.9.

Analysis of Reference Material SLRS-1, and NBS 1643a for Trace Metals

Metal	SLRS-1 Certified ($\mu mol \cdot m^{-3}$)	SLRS-1 Found ($\mu mol \cdot m^{-3}$)	NBS 1643a Certified ($ng \cdot g^{-1}$)	NBS 1643a Found ($ng \cdot g^{-1}$)	Blank[a] (ng)	Detection Limit 3s ($\mu mol \cdot m^{-3}$)	Quantitation Limit 10s ($\mu mol \cdot m^{-3}$)
As [b]	7.34 ± 1.07	4.58 ± 0.0 (4)	77 ± 7	78 ± 10 (3)	2 ± 0.37 (3)	0.15	0.49
Cd [a]	0.134 ± 0.018	0.178 ± 0.045 (4)	10 ± 1	10 ± 2 (3)	0.4 ± 0.1 (4)	0.026	0.09
Cu [b]	56.3 ± 4.7	60.0 ± 3.5 (4)	18 ± 1	20 ± 2 (3)	< 300 (4)	3.0	10.0
Cr [a]	6.92 ± 0.77	8.0 ± 0.9 (4)	15 ± 1	17 ± 2 (3)	< 50 (4)	0.77	2.57
Ni [a]	18.2 ± 1.0	19.6 ± 1.7 (4)	55 ± 1	64 ± 3 (3)	< 100 (4)	1.2	4.0
Pb [a]	0.512 ± 0.053	0.492 ± 0.040 (4)	27 ± 1	31 ± 3 (3)	< 5 (3)	0.30	1.00
V [a]	12.9 ± 1.8	37.7 ± 5.5 (4)	53 ± 1	60 ± 2 (3)	< 500 (4)	12.	40.
Zn [b]	20.5 ± 3.1	20.4 ± 4.0 (4)	72 ± 3	78 ± 4 (3)	< 100 (3)	1.5	5.0
Hg [c]	-	-	-	-	0.5 ± 0.15 (4)	0.009	0.030

a) Blanks estimated from concentrated sample for empty beaker evaporated in same way, taken up in 10 mL Milli-Q water and Seastar HNO_3 (0.1%).

Detection limits assume a 10 x concentration factor (100 mL - > 10 mL) where blank is below detection, based on uncertainty in intercept of calibration curves.

b) Detection limit based on unconcentrated sample

c) Detection limit based on 250 mL of sample

Values given as mean ±1 standard deviation.

Numbers in brackets indicate number of replicates.

Table 2.10.

Combined Analytical, Sampling and Storage Precision of Trace Metal Analyses

Metal	Average Precision (mean of percent standard deviation for triplicate samples, 1985 and 1986)
As	22% (1985) 10% (1986)
Cd	13%
Cu	5%
Cr	20%
Hg	24%
Ni	7%
Pb	8%
V	11%
Zn	16%

2.2.5 Hydrocarbons

2.2.5.1 Materials

a) Apparatus

Virtis homogeniser	Model 45, 250 mL fluted glass flasks stainless steel blades.
Balances - analytical	Sartorius Model 2434, 0.01 mg, 160 g capacity. Oertling R51, 0.01 mg, 80 g capacity.
Balances - top loading	Sartorius 1212, 0.01 g. Sartorius 1264, 0.01 g. Sybron Digimetric, 0.01 g, 2 kg capacity.
Electrobalance	Perkin Elmer AD-2, 0.1 g, 1 g capacity.
Balance calibration weights	Class P standard weights.
Glassware ovens	Blue Model POM60, 340°C forced air oven.
Muffle furnace	Temco, 1200°C.
Gas chromatographs	Hewlett Packard models 5830A and 5840A each with twin flame ionisation detectors (FID), fused silica capillary column, split/splitless injector and integrating printer/plotter.
Gas chromatograph	Hewlett Packard model 5830A with electron capture detector and FID, fused silica column, split/splitless injector and integrating printer/plotter.

Gas chromatograph/ mass spectrometer	Finnigan 9500/3200, fused silica capiliary column directly coupled into spectrometer, electron impact ion source. Finnigan 6100 interactive data system.
Fluorometers	Turner Designs model 10 with short wavelength filters (excitation: 10-038 254 nm, emission: 10-300, 10-064, 7-60, 350 nm), quartz cuvette, 2 x 8 cm, 25 mL capacity.
Rotary evaporators	Buchii R110 with electrically driven recirculating aspirator vacuum pump.
Vacuum filters	Millipore holder YY2214230, stainless steel pressure filter holder, 1/2" NPT inlet and outlet fittings, for 142 mm filters.
	Millipore model XX15047, all glass vacuum filter system for 47 mm filters.
Vacuum pump	Gast oilless vane pump.
Constant temperature bath	Jubalo P20B.
Drying oven	Lab Line Heat Cab, 40-200°C.
XAD column elution system	Seastar Instruments, Teflon fittings and 250 mL glass solvent reservoir.
XAD column cleaning system	Recirculating pumped solvent systems supplied by 5 L soxhlet extractor reservoir, using methanol and dichloro-methane.

b) Glassware

Separatory funnels	4 L Pyrex with glass stopcock.
	1 L Pyrex with Teflon stopcock.
Chromatography columns	10 x 150 mm glass columns, 50 mL reservoir, Teflon stopcock, course glass frit.
Measuring cylinders	2 L polyethylene and 50 mL to 1 L glass.
Vials	4 mL capacity with FEP Teflon screw cap liners.

Ampoules	10 mL borosilicate breakneck style ampules.
Syringes	1.0 µL 801RN removable needle with handle.
Volumetric flasks	50 and 100 mL grade A, with glass stoppers.
GC columns	15 m x 0.25 mm fused silica column with 0.25 µm DB-5 bonded phase J & W Scientific.
	25 m x 0.22 mm fused silica column with 0.25 µm BP-5 bonded phase, SGE.
Pipettes	1.00 mL to 50.00 mL borosilicate grade A.
Soxhlet extractor	100 mL and 250 mL capacity.
Filters	Gelman AE 142 mm glass fibre filters, nominal 1.0 µm retention.
	Whatman GF/C 47 mm glassfibre filters, nominal 1.4 µm retention.
Pasteur pipettes	disposable, 9".
Centrifuge tubes	15 mL Pyrex, graduated to 100 µL with standard ST13 glass stoppers.
Water sample bottles	4.5 L soda glass bottles with FEP Teflon lined screw caps.
Vacuum filter flask	4.5 L Pyrex graduated heavy wall vacuum flask.
Solvent stills	5L Pyrex distillation apparatus, with 90 cm x 2 cm burle packed glass fractionation columns.

c) Solvents and Reagents

Methanol	Caledon, distilled in glass.
Dichloromethane	BDH Omnisolv, distilled in glass.
Hexane	Burdick and Jackson, distilled in glass.
Pentane	Burdick and Jackson, distilled in glass.
Acetone	BDH Omnisolv, distilled in glass.

Freon 113 (1,1,2-tri-fluoro-trichloroethane)	BDH Omnisolv, distilled in glass.
Diethylether	Caledon, distilled in glass, fractionally redistilled before use and stored in refrigerator.
Sodium sulphate anhydrous granular	Baker Chemicals, reagent grade.
Silica gel	BDH, 60-120 mesh, chromatography grade.
Florisil	Baker Chemical 60-100 mesh chromatography grade.
Chromic acid	15 mL "Chromerge" in 4 L concentrated H_2SO_4.
XAD-2 Macroreticular resin	Rohm-Haas Ltd.
Distilled water	All glass still fed by de-ionised reverse osmosis (Millipore RO4) water.
Saturated sodium chloride solution	Extracted with dichloromethane before use.
Helium, Argon:methane	High purity, Canadian Liquid Air Specialty Gases.
Hydrogen	High purity, Canadian Liquid Air.
Nitrogen	K grade.
Compressed air	Medical grade.

d) Standards

Normal alkanes	nC10 to nC36 Analabs, Sigma Chemicals, Altech, PolyScience Corp and Aldrich; as pure liquids and crystaline solids, used as received.
Polycylic aromatics	naphthalene to perylene, Aldrich, Eastman Chemicals, Sigma Chemicals, crystaline standards, used as received.
Internal standards	5 alpha-androstane, hexatriacontane-d_{74}, 2-methylnaphthalene-d_{10} and perylene-d_{12}; used as received from MSD Isotopes as pure liquid or crystaline standards. Naphthalene-d_8, fluorene-d_{10}, pyrene-d_{20}, chrysene-d_{10} and

	benzo(b)fluoranthene-d_{12} provided by MSD. Isotopes as a composite standard in benzene-d_6 (Standard MW-2768, Base-neutrals 6.2).
Chlorinated hydrocarbons	PCB (Aroclor 1254), decachlorobiphenyl, Lindane, heptachlor, heptachlorepoxide, cis and trans chlordane, o,p'-and p,p'-DDT, DDE and DDT, endrin, dieldrin, alpha- and beta-endosulphan, Mirex, alpha-BHC, gamma-BHC supplied as pure liquids or crystalline solids and used as received from Agriculture Canada, Food Production and Inspection Branch, Ultra Scientific, Foxboro/Analabs and Aldrich Chemicals.
Reference Materials	PAH certified standard NBS SRM 1647. 16 PAHs supplied as a certified concentration in acetonitrile.
	NRCC marine sediment reference materials CS-1, HS-1, and HS-2; poly-chlorinated biphenyls in marine sediments.

e) Blanks and Standardization

Solvent blank run for each new bottle of solvent before use to check for interference and determine blanks.

Procedural blank carried through each analysis every six samples.

n-alkanes by GC/FID	Basaeline run initially each working day.
	Calibration standard including internal standard run daily. Relative response factors rcorded in log file.
	Internal standards (5 alpha-androstane and hexatriacontane-d_{74}, nC36-d_{74} added to each sample prior to work up.
PAH by GC/MS	Calibration, standard run daily before and after samples to monitor instrumental stability. Multiple internal standards added to each sample prior to work-up.
PAH by UV-fluorescence	The fluorometer was standardized daily using a series of standards (Norman Wells crude in hexane) and the sampel cuvette rinsed repeatedly between samples until the blank was indistinguishable from the solvent blank.

Chlorinated hydrocarbons by GC/ECD	Baseline and solvent baseline run initially each working day. Calibration standards for PCBs and 14 selected chlorinated hydrocarbons run each day.

f) Preparation of Apparatus and Reagents

Solvent purity	Only distilled in glass, pesticide grade solvents used, each bottle checked for contamination before use. Diethylether redistilled through a fractionation column before use.
Glassware	Washed in lab detergent, rinsed with tap water then distilled water, air dried and baked overnight at 340°C in a forced air oven immediately before use. Glassware wrapped in aluminum foil for storage. In addition, glassware solvent rinsed (acetone, dichloromethane, then hexane) when oven baking not possible. Small items baked at 500°C overnight in muffle furnace.
Metal and Teflon items	Detergent wash, distilled water rinse, dried with acetone and cleaned with dichloromethane and hexane.
Sodium sulphate	Baked overnight at 500°C, stored in ground glass stoppered bottle.
Silica gel	Washed with methanol dried at 60°C 48 h, then activated at 500°C 24 h. Allowed to cool in stoppered flask and deactivated with 3% water by weight. Allowed to stand 48 h before use.
Florisil	Washed with water and methanol, dried at 60°C 48 h then activated at 500°C 24 h. Cooled and deactivated with 3% distilled water, by weight, in a stoppered flask. Allowed to stand 48 h before use.
filters	47 mm glass fibre filters (Whatman GF/C) were baked at 500°C, 18 h and stored in baked aluminum foil pouches. Gelman 142 mm AE filters were baked at 340°C 12 h and stored in baked aluminum foil pouches.

FEP Teflon cap liners	Cleaned overnight in chromic acid, washed and rinsed in tap water and distilled water, rinsed with acetone and dichloromethane and stored in cleaned aluminum foil pouches before use.

2.2.5.2 Hydrocarbon Analyses

Procedures for analysis of the first suite of samples were designed primarily for UV fluorescence, but were subsequently changed to GC based methods for the 1986 samples to improve the detection limit and focus on the components of interest. Consequently there were some changes in procedures between the 1985 and 1986 sample analyses.

a) Water Filtration and Extraction

Most water samples collected by NBS drop sampler were transported back to Sidney, B.C. for processing. The suite of samples collected in February 1986 however, were filtered and extracted at the Inuvik Research Laboratory, as well as a number of water samples from April 1985 which were filtered in the field. Essentially the same procedures and equipment were used throughout the project although 4 L samples were processed individually in April 1985. Also, high temperature glassware cleaning procedures were not possible for processing carried out in Inuvik or in the ice hut on the river.

Water samples (4-5 L, April 1985 or 18-19 L in 4 x 4.5 L water bottles, February 1986) were shaken thoroughly to resuspend material separated during sample storage then vacuum filtered through a 142 mm glass fibre filter (Gelman AE) into a graduated 4 L vacuum filter flask. The filtered water was returned to the sample bottle and subsequent subsamples filtered. Two 250 mL subsamples were also filtered for duplicate particulate organic carbon analysis during the winter field program. Glass fibre filters were folded to retain collected particulate and stored at -20^{o}C in prebaked or solvent rinsed aluminum foil pouches for UV-fluorescence and GC analysis.

The filtered water was serially extracted in 4 L subsamples with hexane (100 mL, 50 mL and 50 mL, April 1985) or dichloromethane (200 mL, 100 mL and 100 mL, February 1986) and where necessary successive extracts stored in separate 250 mL erlenmeyers until the entire sample (4 L April 1985, 18 L February 1986) had been extracted. The volume of the first extract was made up to 200 mL before use for further extraction to compensate for solubility losses. After extraction of the entire

sample, the extracts were combined, dried over anhydrous sodium sulphate, taken down to 25 mL by rotary evaporation at 25°C and analyzed by UV-fluorescence (April 1985) or taken down to 2 mL for GC analysis (1986). Samples extracted in Inuvik were sealed into 10 mL breakneck ampoules for shipment to Sidney.

b) Filter and Centrifuged Sediment Extraction

Filters from 1985 4 L water filtrations and in situ sample filters were extracted by homogenisation with a Virtis homogeniser for 5 minutes in hexane (3 x 40 mL) and the extracts taken down to 20 mL for immediate analysis by UV-fluorescence.

Filters from the 1986 program, in situ sampler filters and suspended material separated by continuous-flow centrifuge were extracted, without drying, for hydrocarbons and chlorinated hydrocarbons by the following procedure. The sample was spiked with internal standards, and homogenised in a Virtis homogeniser with acetone (50 mL), allowed to stand, the extract supernatant drawn off by pipette and the residue further extracted by homogenisation with dichloromethane (2 x 80 mL). The combined extracts were dried over anhydrous sodium sulphate and taken down to 2 mL by rotary evaporation at 30°C for GC/FID, GC/EC and GC/MS analysis.

Extracted sediment from the continuous-flow centrifuge was further extracted 48 h in a soxhlet with dichloromethane.

c) In Situ Sampler Column Extraction

XAD-2 columns were spiked with internal standards 5 alpha-androstane and $nC36\text{-}d_{74}$ (1 µg of each) and a suite of six perdeuterated PAHs at 0.2 µg each and eluted from bottom to top with methanol (200 mL) and dichloromethane (250 mL). The combined eluate was taken down to 40 mL, shaken with 25 mL saturated sodium chloride solution; serially extracted with pentane (3 x 100 mL), the extract dried over anhydrous sodium sulphate and taken down to 2 mL by vacuum rotary evaporation. Extracts of the spring (1985) samples were displaced into UV grade hexane for UV-fluorescence analysis by the addition of 10 mL hexane blown down to 1 mL by dry nitrogen and made up to 20 mL with hexane in the sample cuvette.

d) Sample Clean-up for Hydrocarbon Analysis

Water, filter, XAD-2 column and continuous-flow centrifuge sediment extracts including those analyzed by UV-fluorescence, were separated into nonpolar and aromatic fractions. The extracts were blown down to 1 mL with dry nitrogen, applied to a silica gel column (10 x 150 mm, 3% water deactivated capped with 10 mm anhydrous sodium sulphate), and eluted with hexane (25 mL, F1, nonpolar hydrocarbons) and dichloromethane (40 mL, F2, aromatic hydrocarbons). Fractions were taken down to 100 µL by rotary evaporation and dry nitrogen jet evaporation and analyzed by GC/FID and GC/MS, respectively.

e) Sample Clean-up for Chlorinated Hydrocarbon Analysis

Two column extracts, an in situ sampler filter extract, and a continuous-flow centrifuge sediment extract, were separated by liquid chromatography for chlorinated hydrocarbon analysis. The extracts were blown down to 1 mL, applied to a florisil column (10 x 200 mm, 5% water deactivated, capped with a 1 cm layer of anhydrous sodium sulphate slurry packed in hexane) and eluted with 37 mL hexane, 37 mL 6% diethylether in hexane and 37 mL 15% diethylether in hexane. The following fractions were collected F1 (27 mL), F2 (47 mL) and F3 (37 mL) which were taken down to 100 µL and analyzed immediately by GC/ECD.

2.2.5.3 Instrumental Conditions

Nonpolar hydrocarbons were determined using Hewlett-Packard 5830A/5840A gas chromatographs with flame ionisation detectors (FID) operated with the following instrumental conditions:

Column: 25 m x 0.22 mm BP-1 bonded phase fused silica column, (SGE), or 15 m x 0.25 mm DB-5 bonded phase fused silica column (J&W Scientific).

Carrier: Hydrogen at 14-18 psi, 1 mL·min-1 nominal flow rate.

Injector: Grob type, split/splitless, 250° C, splitless 1.0 µL injections, split resumed 1.0 min after injection.

Detector: FID at 350° C, hydrogen 30 $mL \cdot min^{-1}$, air 240 $mL \cdot min^{-1}$, nitrogen (make up) 30 $mL \cdot min^{-1}$.

Program: Initial oven temperature 50° C, held for 1.0 min, oven heated at 10 $C^{o} \cdot min^{-1}$ to 300° C and held for 10 min.

Peak areas were measured using the HP 5834/40 integrator and compounds were quantified relative to the primary internal standard, perdeuterated nC36. An additional internal standard, 5 alpha-androstane, was present as a back-up quantification standard in the event of interference at the primary standard.

An even n-alkane calibration standard was run at least once a day and relative response factors calculated relative to predeuterated nC36.

Concentrations are reported in $ng.L^{-1}$ for the following nonpolar hydrocarbons; n-alkanes (nC10 to nC38), isoprenoid alkanes (pristane, phytane, farnesane, norpristane and trimethyltridecane).

Aromatic fractions were analyzed on a Finnigan 9500/3200 gas chromatograph-mass spectrometer (GC/MS), with a Finnigan 6100 data system using the following conditions:

Column:	25 m x 0.25 mm BP-5 bonded phase fused silica column (SGE, Australia).
Carrier Gas:	helium
Injector Flow Rate:	60 $mL \cdot min^{-1}$
Injector Pressure:	17 p.s.i.g.
Column Flow:	40 $cm \cdot s^{-1}$
Split Ratio:	40:1 (approximately)
Injector Temperature:	260°C
Injection Sequence:	splitless injection at room temperature, splitting resumed at 1 minute, 100° C at 2 minutes and 10 C° min^{-1} at 4.5 minutes to 280°C and hold for 10 minutes. 0.5 µL injections.
Mass Spectrometer:	electron impact source
Source Emission:	0.50 mA
Electron Energy:	40 eV
Operating Pressure:	1×10^{-5} torr
Multiplier Voltage:	2000 V (gain > 10^6)
Data Acquisition:	data acquired in the "selected ion monitor" mode with one scan per sec; four ions per scan in five clusters of four ions per run. Data archived on magnetic tape.

Peak areas were measured by manually controlled integration on the 6100 data system.

Chlorinated hydrocarbons were determined using a Hewlett Packard 5830A gas chromatograph, with a ^{63}Ni electron capture detector and a 30 m x 0.25 mm DB5 Durabond Fused Silica capillary column (J & W Scientific). The following conditions were used:

Carrier Gas:	Hydrogen: 60 mL·min^{-1}, approximate 40:1 split ratio
Make-up Gas:	Argon with 5% methane; 30mL·min^{-1}
Injector Temperature:	250 °C
Detector Temperature:	300 °C
Oven Temperature:	Held 100°C for one minute, then programmed 100 °C to 180°C at 20 C° min^{-1} then 10 C° min^{-1} to 270°C, and held for 5 min.
Syringe:	Hamilton 10 µL syringe
Injection mode:	Grob splitless injection, carrier splitting resumed after three minutes
Injector Pressure:	12 psi (split), 37 psi (splitless)

A baseline and injection blank (i.e., solvent injected) and calibration standard were run at the start of each daily use of the GC.

a) Assignment of GC/ECD Chromatograms

A peak is assigned to a given chlorinated compound only if all of the following criteria are satisfied:

(a) The corrected retention time is within ±0.02 minutes of that expected.

(b) Upon co-injection with the authentic material, the sample and standard compounds co-elute as one peak.

(c) The compound is expected in that Florisil column fraction injected.

(d) The GC peak shape resembles that of the authentic compound.

A composite pesticide standard and a PCB standard (Aroclor 1254) was run daily to verify instrument performance, establish current retention times and determine current response factors.

Each sample fraction was injected in duplicate, then co-injected with a pesticide composite standard mixture.

b) UV-fluorescence Analysis

Extracts were analyzed by UV-fluorescence using a Turner Designs model 10 fluorometer with the Turner short wave length oil detection filter kit. The instrument was calibrated with a series of dilutions of Norman Wells crude oil standards in hexane from 5 $mg \cdot L^{-1}$ to 0.5 $\mu g \cdot L^{-1}$.

Samples were run at two or more gravimetrically determined dilutions in hexane to verify that the fluorescence measurements were made in a linear, unquenched response region.

2.2.5.4 Quality Control and Quality Assurance

a) Reagents and Glassware

Organic analysis at trace levels is impossible without scrupulously clean glassware and reagents. Consequently particular emphasis was placed on obtaining minimal and consistent blank residual levels for procedural, solvent and reagent blanks. Acceptable blanks were obtained using the following procedures. Glassware was cleaned by the usual methods then baked at 340°C overnight in a forced air oven, before use. Gelman filters were heated at 340°C overnight. Other glass fibre filters were heated to 500°C overnight. All solvents were "distilled in glass", pesticide grade and were checked before use.

b) UV-fluorescence Analysis

The instrument was calibrated using a series of eight standards of Norman Wells crude oil in UV grade hexane (63 $mg \cdot L^{-1}$ to 0.105 $mg \cdot L^{-1}$ by weight) and the calibration checked at two points regularly during each working day. Fluorescence response was linear with concentration to 6 $mg \cdot L^{-1}$, which was defined as the limit of the working concentration range. Between measurements, the quartz cuvette was thoroughly solvent rinsed until the mean solvent blank value (corresponding to 0.10 ±

0.04 $mg \cdot L^{-1}$ Norman Wells crude equivalents) was observed. Samples were run at two or more dilutions to confirm that the measured concentration was within the linear range.

A standard addition procedure with aliquots of a chrysene standard (12.0 ug) was used to determine the PAH extraction efficiency from 142 mm glass fibre filters using UV-fluorescence to quantify the recovered chrysene. The mean recovery and extraction efficiency was 81±3%.

c) GC/FID Analysis of Nonpolar Hydrocarbons

The instrument response was determined daily with a calibration standard from which a set of response factors, relative to the internal standard, was calculated for each of the compounds of interest. Chromatograms were quantified using target compound and internal standard peak areas.

No suitable standard reference material was available for the verification of the nonpolar hydrocarbon analyses, but subsamples of two continuous-flow centrifuge sediments have been submitted for independent analysis by Dr. Walter Cretney, Ocean Chemistry Division, at the Institute of Ocean Sciences, Patricia Bay, B.C. These results are not yet available.

d) GC/MS Analysis of Polar Hydrocarbons

The MS response and resolution were optimised daily using perfluorotributylamine (FC43) using primarily the 219/220 peaks. The data system was mass calibrated daily using FC43.

The precision of the GC/MS SIM analysis is dependent on the maintenance of stable relative response factors. Consequently, the GC/MS was calibrated at the start and end of each working day and the sample data collected for that day accepted only if the relative response factors varied by less than 10%.

The performance of the GC/MS was determined periodically by comparison of the ion abundances of the mass spectrum of decafluorotriphenylphosphine (50 ng) with accepted published values (Eichelberger, 1979).

Instrumental linearity was determined by the triplicate analysis of a suite of PAHs of interest at three concentrations covering a range of two orders of magnitude, including the normal working range, spiked with a constant level of internal standard. The results indicate good linearity in the range of interest.

Seven perdeuterated PAH internal standards are used in these analyses to minimise errors from discrimination or evaporation and to improve the accuracy of peak assignments.

There is no directly applicable certified standard reference sediment for aromatic hydrocarbons in fluvial sediments but a certified reference material (U.S. National Bureau of Standards, SRM 1647) consisting of an acetonitrile solution of several PAHs was analyzed. The results for these analyses are given in Table 2.11 and indicate acceptable accuracy for these compounds.

2.3 Statistical Methods of Data Analysis

Results from dissolved nutrients, suspended particulate material, trace metals and particulate hydrocarbons were analyzed statistically using the statistical program SYSTAT (Systat Inc., Evanston, IL.) for significant differences over the time series, by depth, by cross channel location, by year and by channel. For each parameter, an analysis of variance (ANOVA) and Bartlett's test for homogeneity of variance (Sokal and Rohlf, 1969) were performed to determine if differences for each parameter were significant at a 95% probability level. An ANOVA for the time series data set at East Channel, location 5 (centre hole), 5 m depth in 1986 indicated no significant change over time, and subsequently the time series results were treated as replicate sets. Similarly ANOVAs were run by depth, by cross channel location, and by year for the East Channel and data sets which indicated no significant differences for these variables were then treated as replicate sets.

Table 2.11.

Analysis of Certified Reference Material for PAH
(NBS Standard Reference Material SRM 1647.
Acetonitrile solution of several PAHs.)

Compound	Certified ($ng.L^{-1}$)		Found ($ng.L^{-1}$)	
naphthalene	22.5	±0.2*	16.0	22.3
fluorene	4.92	±0.1	3.74	6.5
phenanthrene	5.06	±0.1	3.96	5.5
anthracene	3.29	±0.1	3.04	3.8
fluoranthene	10.1	±0.2	11.4	10.5
pyrene	9.8	±01	13.7	10.0
benz(a)anthracene	5.03	±01	4.40	4.8
chrysene	4.68	±0.1	4.40	5.1
benzofluoranthenes	10.2	±0.2	12.1	10.0
benzo(a)pyrene	5.3	±0.1	5.7	5.4

* estimated uncertainty

3. RESULTS AND DISCUSSIONS

3.1 Discharge Calculations

The cross-sectional current field in the East channel in 1985 is shown in Figure 3.1. Maximum currents were about 32 $cm \cdot sec^{-1}$ at a depth of 1.5 - 4 m under the ice and about 160 m from the east side of the channel. Current speed did not appear to vary appreciably during the sampling period as indicated by 3 h time series measurements at location 5 (fluctuations in current speed were less than 10%) and the record from the moored meter (Figure 3.2). The moored meter indicated a uniform flow with no detectable tidal influence. Current speed fluctuated between 15 - 20 $cm \cdot sec^{-1}$. There had been some question of whether during the lower flows of the winter months there might be a tidal effect or possibly an intrusion of saline shelf water into the channel. The meter was moored near the bottom for this reason. The current data (and salinity data) indicated clearly that this did not occur.

The flow through the channel was calculated as 1080 $m^3 \cdot sec^{-1}$ during this period. The flow (Q) was computed using the formula:

$$Q = \sum_{i=1}^{10} b_i \mu_i h_i$$

where:

b_i = width of the section (10 sections across channel, 60 m for each side section, 40 m for the rest);

μ_i = the current speed in section i, taken as the mean of the current profile in the section; and

h_i = the depth taken as mean water depth under the ice in section i.

Cross-sectional current profiles for each channel in February 1986 are shown in Figure 3.3(a) and 3.3(b). Maximum currents were observed in the Main Channel (30 $cm \cdot sec^{-1}$) and in the East Channel 33 $cm \cdot sec^{-1}$. Currents were slower in Reindeer (max speed 21 $cm \cdot sec^{-1}$) and Middle (max speed 18 $cm \cdot sec^{-1}$) Channels. The flow through each channel was computed as in 1985.

Discharge calculations are summarized in Table 3.1 and compared with Inland Waters Directorate (IWD) data and historical data from the Main Channel in 1975 and 1976. The IWD data for the Main Channel suggest that flows were lower in 1986 than in the mid 1970's. The discharge values also indicate that virtually all the flow

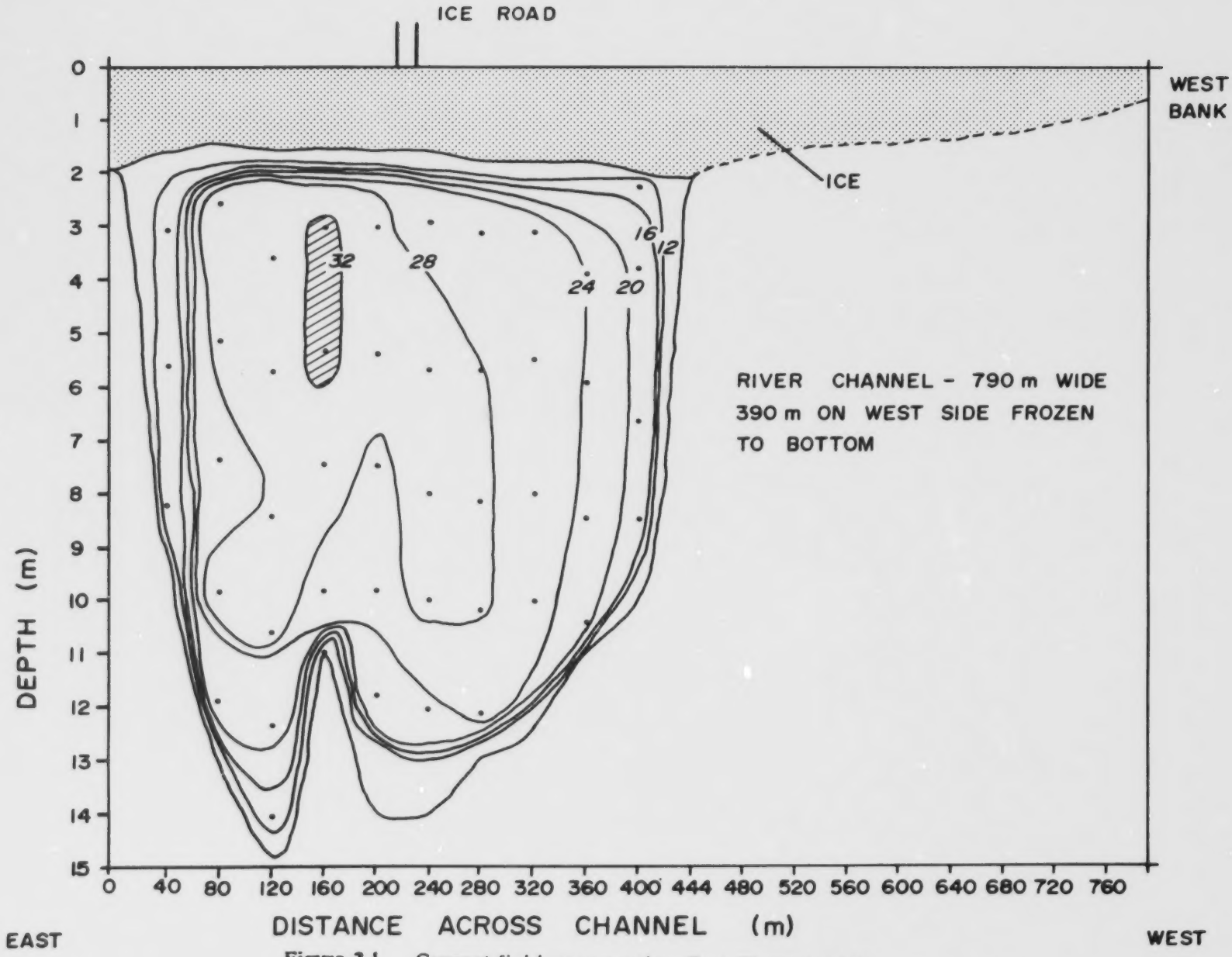


Figure 3.1 Current field cross-section, East Channel, 1985.

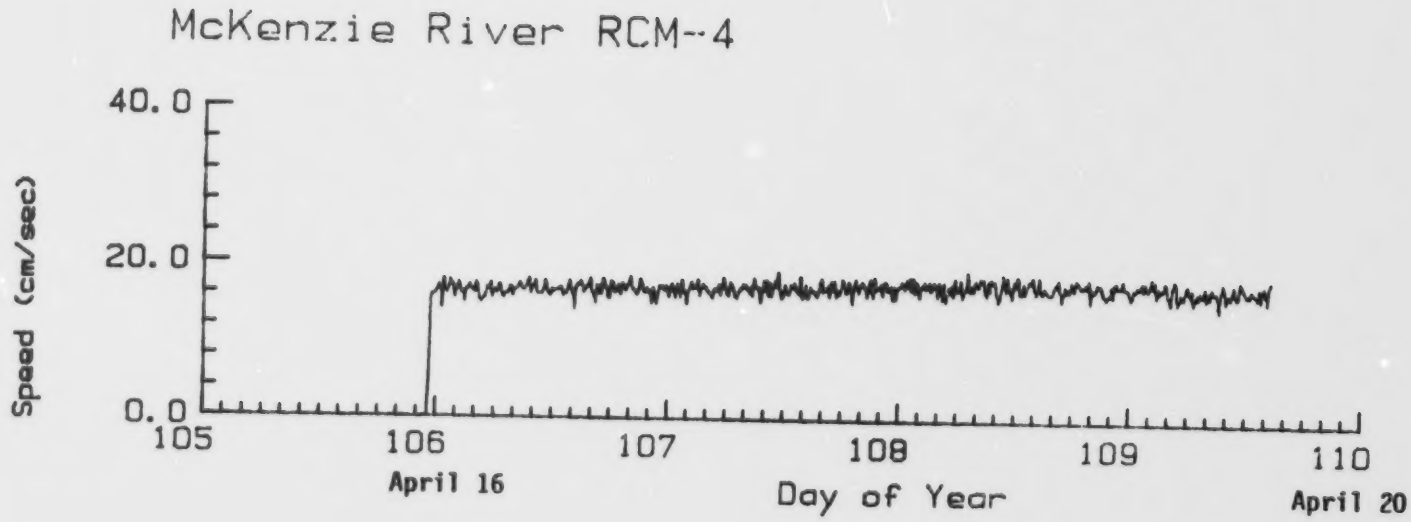


Figure 3.2 Record from moored RCM-4 25 km downstream from Swimming Point, April 1986.

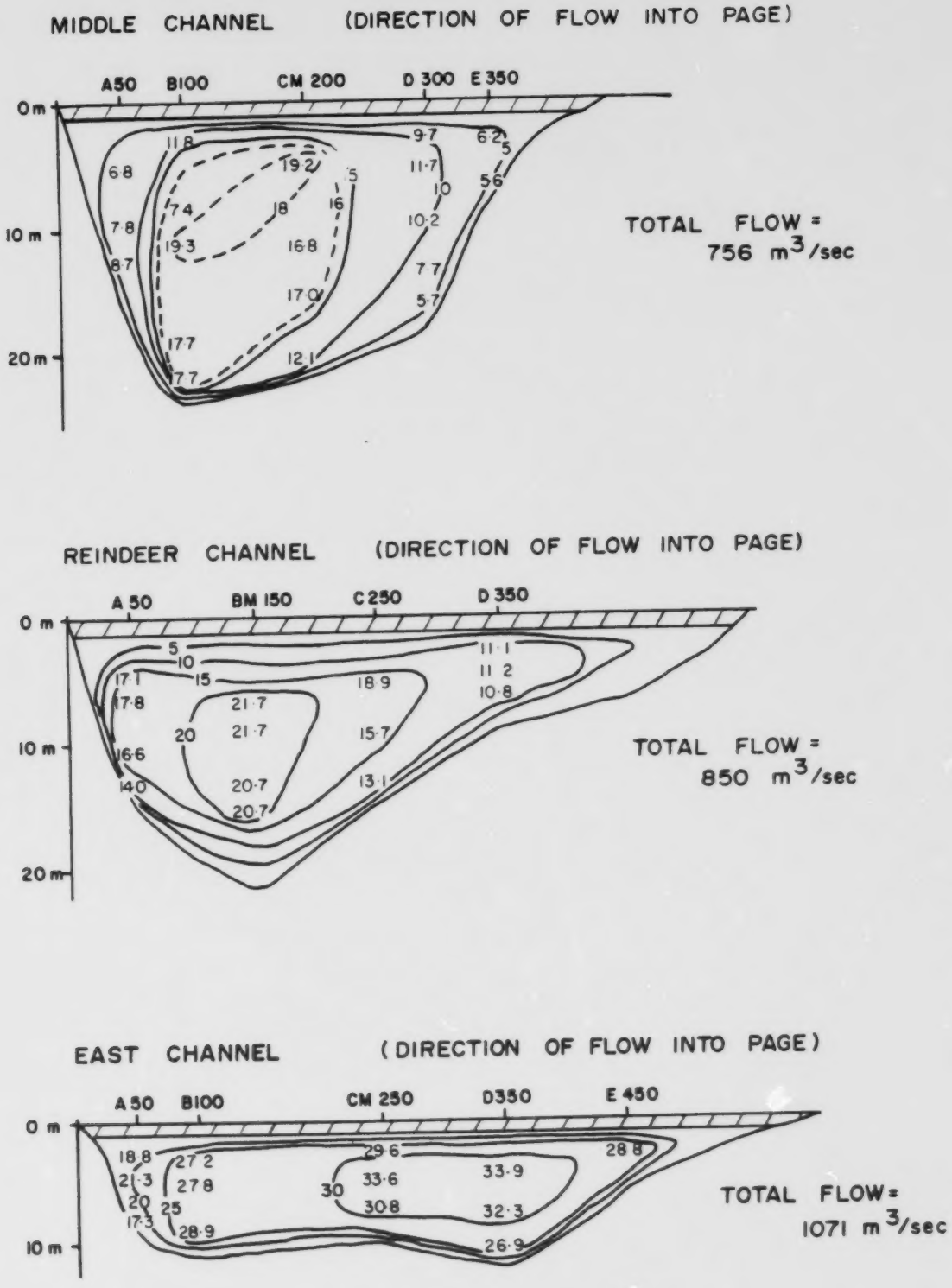


Figure 3.3(a) Current field cross-sections, Middle, East and Reindeer Channels, February 1986.

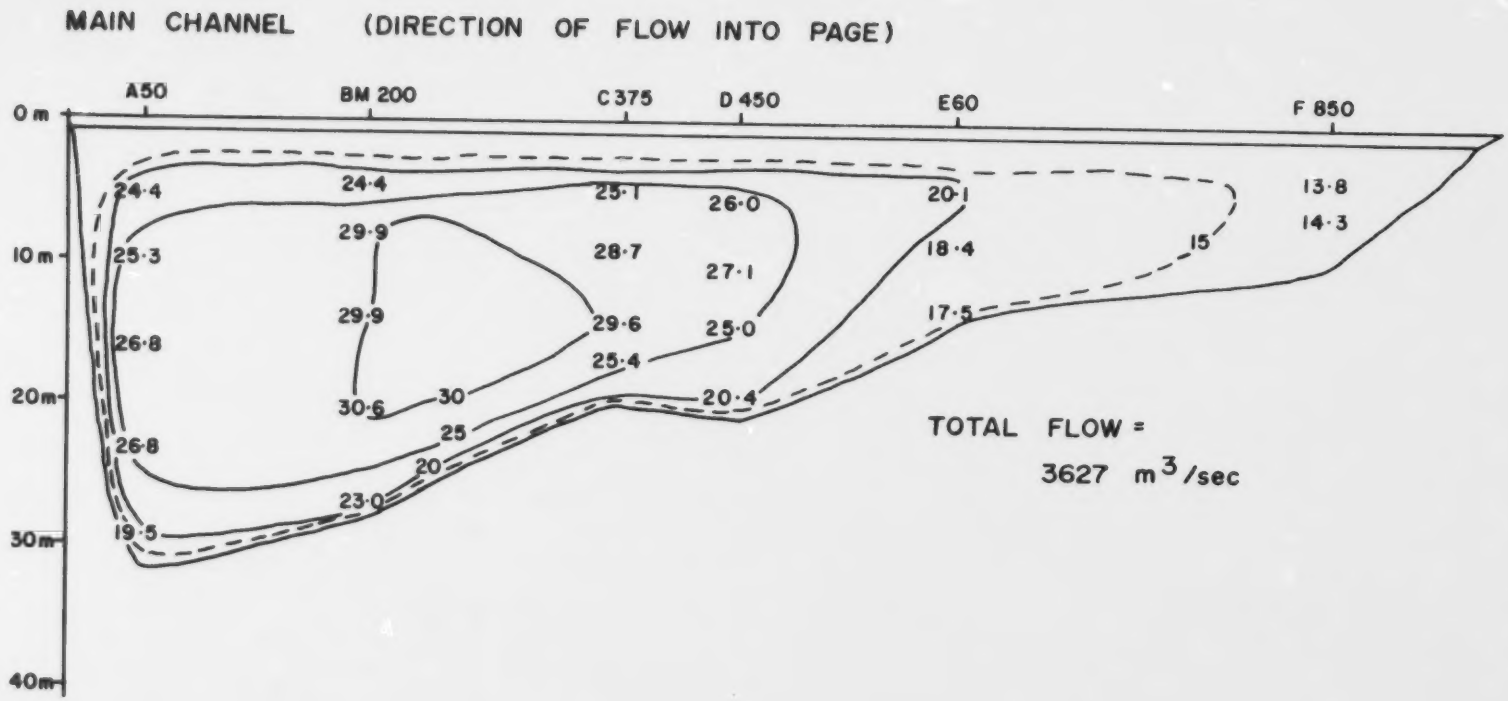


Figure 3.3(b) Current field cross-section, Main Channel, February 1986.

Table 3.1.

Summary of Channel Discharge Measurements
($m^3 \cdot sec^{-1}$)

Location	Month	Year	This Study	Inland Waters Directorate
Main Channel	February	1975	-	4090
	March	1976	-	3600
	February	1986	3627	2820
East Channel	April	1985	1086	1180
	February	1986	1071	1130
	March	1986	-	1040
Reindeer Channel	February	1986	850	988
Middle Channel	February	1986	756	691
Total of East, Reindeer and Middle Channel		1986	2677	2809

in the Main Channel is accounted for by the combined flows through the East, Reindeer and Middle Channels. The less detailed measurements made in this study give a higher flow for the Main Channel and a combined flow in the outer three channels which is only 74% of the flow through the Main Channel. The poor agreement between the flow in the Main Channel obtained in this study compared to that by IWD is partly explained by the number of verticals at which measurements were taken. Only 6 verticals were measured in this study compared to 20 by IWD. The smaller number of verticals will increase the error in discharge measurement because of the wider channel and less uniform cross-channel depth profile (Jansen et al., 1979).

3.2 Suspended Particulate Material (SPM)

3.2.1 Weight

Results for total SPM (>0.4 μm) are presented in Table 3.2 for the East Channel in April 1985 and in Table 3.3 for all four channels sampled in February, 1986. The means of all data for the East Channel in April 1985 and February 1986 are the same given the uncertainty of the measurements (4.71 ± 0.65; 4.83 ± 0.88 $mg \cdot L^{-1}$). The high variability observed in duplicate samples from the same depth in 1986 at some locations and depths suggests that settling of particles in the sampling bottle or problems in storage may have been a factor. The results indicate a relatively homogenous SPM in the January to April period while flows are at their annual minimum.

SPM levels in the Main Channel were higher than in the three outer channels indicating that settling was taking place downstream. Concentrations vary directly with current speed in the three outer channels. The total flux of suspended solids through each channel in February 1986 using IWD discharge data is summarized below:

Channel	Mean SPM $g \cdot m^{-3}$	Discharge $m^3 \cdot sec^{-1}$	Flux $kg \cdot sec^{-1}$
Main	6.53	2820	18.4
East	5.15	1130	5.82
Reindeer	4.89	988	4.83
Middle	4.58	691	3.16
Total of Outer Channels		2809	13.81
Difference			4.59

Table 3.2.

Suspended Particulate Material (SPM)
East Channel, April 16-19, 1985

Station	Date	Depth	SPM $g \cdot m^{-3}$ (dry weight)
5	16/04/85	2	4.48
	17/04/85	5	5.14, 4.83, 5.31, 4.99 ($\bar{x}$ = 5.07 ±0.21)
	17/04/85	8	3.72
1	19/04/85	4	4.16
2	18/04/85	7	5.05
3	19/04/85	4	5.31
4	18/04/85	5	5.47
6	18/04/85	5	5.47
7	18/04/85	6	4.64
8	18/04/85	5	5.37
9	19/05/85	4	5.30
10	19/05/85	4	4.25

Mean all data (simple average) = 4.71 ± 0.65 $g \cdot m^{-3}$

Table 3.3.

Suspended Particulate Material (SPM)
Main, Middle, East and Reindeer Channels,
February 1 - 8, 1986

Channel:	Date	Location	Depth (m)	Replicate	SPM $g \cdot m^{-3}$ (dry weight)	Mean $g \cdot m^{-3}$
Main:	05/02/86	Centre	5	1	7.50	6.71
				2	5.92	
			10	1	7.14	6.74
				2	6.34	
			20	1	6.53	6.53
				2		
			26	1	5.76	6.18
				2	6.60	
		West	10	1	7.16	6.83
				2	6.49	
		East	8	1	6.27	6.18
				2	6.09	
Middle:	01/02/86	Centre	5	1	4.13	4.16
				2	4.19	
			10	1	4.45	4.48
				2	4.51	
			16	1	4.40	4.61
				2	4.82	
		West	8	1	4.74	4.84
				2	4.94	
		East	8	1	4.76	4.81
				2	4.86	

Table 3.3, cont'd.

Suspended Particulate Material
Main, Middle, East and Reindeer Channels,
February 1 - 8, 1986

Channel:	Date	Location	Depth (m)	Replicate	SPM $g.m^{-3}$ (dry weight)	Mean $g.m^{-3}$
Reindeer:	03/02/86	Centre	4	1	4.42	4.55
				2	4.67	
			10	1	4.50	4.65
				2	4.80	
			18	1	4.96	4.28
				2	3.60	
		West	8	1	5.92	5.40
				2	4.88	
		East	8	1	5.69	5.60
				2	5.50	
East:	07/02/86 1400	Centre	3	1	4.08	5.10
				2	6.68	
			8	*	*	4.88 ±0.31
		West	5	1	4.49	4.53
				2	4.58	
		East	5	1	4.90	5.35
				2	5.79	
	07/02/86 2300	Centre T.S.2	3	1	5.45	5.81
				2	6.20	
	08/02/86 0845	T.S.3	3	1	4.15	5.33
				2	6.49	

* 3 litres collected from a single PVC sampler (East Centre - 8 m) and five aliquots of 500 - 600 mL filtered through five separate filters gave the following results: 4.83, 5.16, 4.44, 5.21, 4.78.

It would appear that about 25% of the total suspended solids >0.4 µm settle out between the Main Channel site and the sites sampled in the outer channels. It is difficult to predict the percentage of particles that might be expected to settle out because of the effects of particle shape, density and turbulence. Simple gravitational settling velocity, based on a current of 30 $cm \cdot sec^{-1}$ and a particle density of about 1.8 $g \cdot cm^{-3}$, would suggest that all particles greater than about 3 µm should settle out over the distance between the Main Channel and outer channel sites. Turbulent diffusion of the particles is generally of equal importance to gravitational transport and is obviously sufficient to keep most particles in suspension. However, further settling of particulates can be expected prior to discharge into the Beaufort Sea as current speeds decrease.

3.2.1.1 Comparison of Continuous-Flow Centrifuge to Filtration

Total dry weight of suspended particulates from the continuous-flow centrifuge was not determined directly as the oven drying step is undesirable before hydrocarbon analysis. The total dry weight SPM collected by the continuous-flow centrifuge was calculated assuming that the water content of the sediment subsample was representative. The comparison with SPM determined by filtration through 0.4 µm Nuclepore filters (Table 3.4) indicates that centrifuge recovery efficiencies are systematically approximately 30% of filter values. The performance specification (Ongley and Blachford, 1982) of the Sedisamp describes the recovery efficiency as a function of SPM concentration and poor recoveries are expected below 15 ppm. Extrapolation of the published Sedisamp recovery efficiency/SPM plot (Ongley and Blachford, 1982) indicates a recovery of less than 40% at 5 ppm SPM, which is consistent with the observed recovery efficiency found in this study.

At constant SPM levels, uniform recoveries are expected from the centrifuge down to 0.4 µm mean particle size, below which recovery efficiency falls exponentially (Ongley, 1986). At an *in situ* mean particle size of 4.5 µm found in this study, the SPM level will control the recovery efficiency. Also, the mean particle sizes determined by Sedigraph for resuspended Sedisamp sediment (< 0.3 µm) are not consistent with the observed recovery efficiency and indicate a more dispersed state than for the *in situ* SPM.

Table 3.4

Comparison of SPM by Filtration and
Continuous-Flow Centrifuge

Channel	Suspended Particulate ($g.m^{-3}$)		
	Centrifuge	Filtration	%[a]
Middle	1.09	4.58	23.9
Reindeer	1.71	4.90	35.0
Main	1.91	6.61	28.9
East	1.69	5.16	32.7

a) % of centrifuge of filtered value.

3.2.2 Particle Size

3.2.2.1 East Channel, April 17-19, 1985

The size distribution of samples collected and analyzed by Coulter Counter in the field or in Inuvik within 12 h of collection are summarized in Table 3.5. Histogram plots are given in Appendix A. For all samples, there was a peak in the size distribution between 2 - 6.5 micrometers.

3.2.2.2 Main, East, Reindeer and Middle Channels, February 1 - 8, 1986

Representative results from each channel are summarized in Appendix B as analyzed with the CMH 150 sensor within 24 h of collection. Samples from all channels, depths and locations were very similar both in population (number) and distribution. The distribution of particles in all channels had a maximum at about 4.0 µm. No particles were found larger than 16 micrometers. Analysis about 4 weeks later indicated similar distributions with peak populations (number of particles) in the range 4 - 8 µm (Appendix B, Figure 3.4). In samples from Reindeer and Middle Channel, (slowest currents) there were small peaks in particle levels at 1.0 µm and 0.6 µm in stored samples although numbers of particles were only about 20-25% of the main peak. These may be due to bacterial growth during storage. There was a shift in maximum particle counts to a larger particle size in some stored samples perhaps as a result of flocculation or possibly because of the different sensor used.

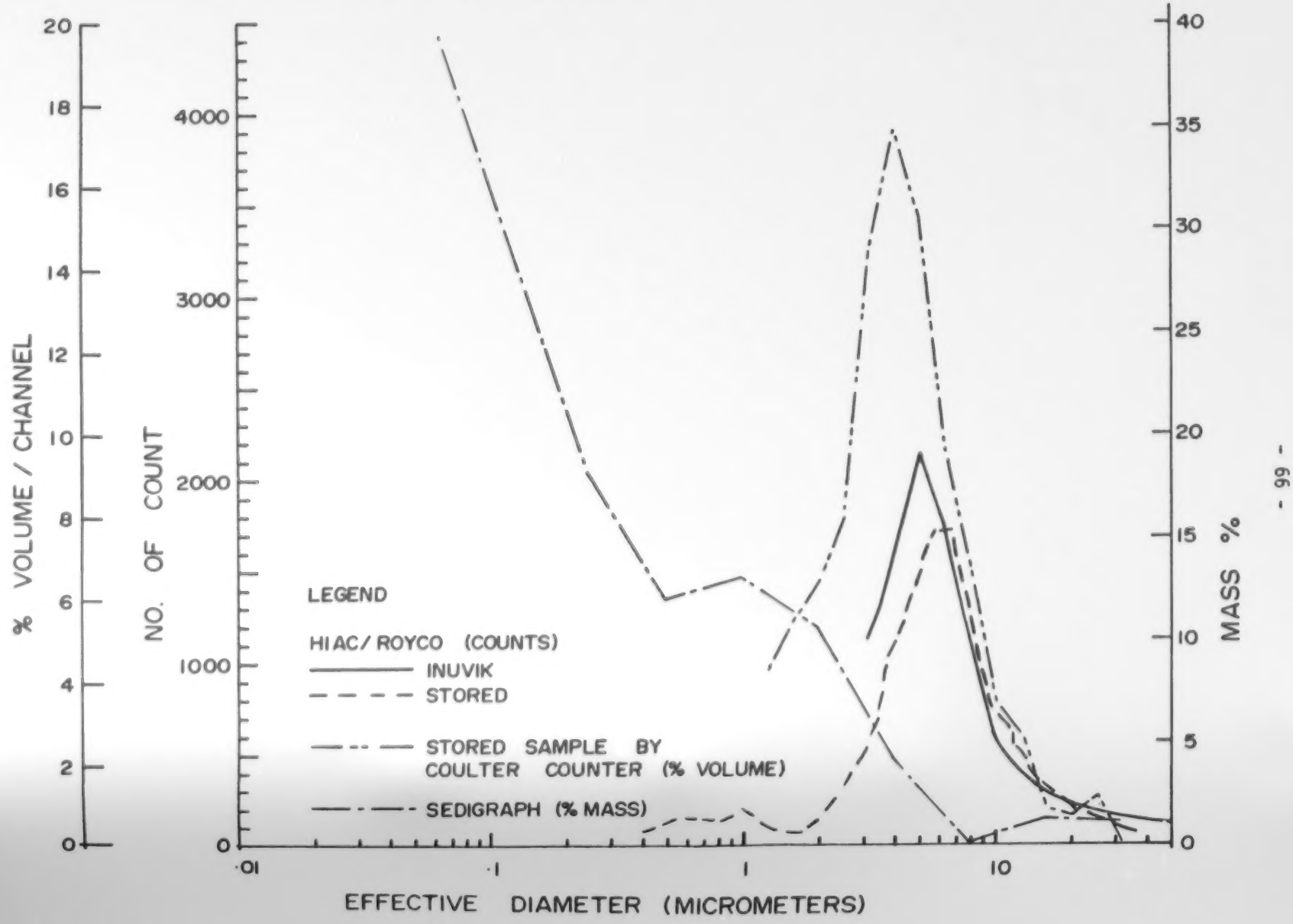
The results of the Sedigraph analysis of the Sedisamp sample from the Main Channel are shown in Figure 3.4. This analysis indicated that 55% of the material was finer than 0.4 micrometers, the cut-off in filtration for total SPM by weight. These results are surprising given the maximum in particle size for the other methods of 3 - 6 µm with very few particles between 0.4 and 1.0 µm. Also, the method of collection (continuous-flow centrifuge) should more efficiently recover larger, more massive particles and the recovery efficiency of the centrifuge is very poor for particles smaller than 0.4 µm. There is a slight maximum in percent mass at about 1.0 micrometer, and in agreement with the other methods, virtually no particles above 15 µm in size.

Table 3.5.

Particle Size of Suspended Particulate Material
by Coulter Counter Analyses, East Channel, April 1985

	Station 2 Depth 7 m	Station 4 Depth 5 m	Station 5 Depth 2 m	Station 5 Depth 5 m	Station 5 Depth 8 m	Station 6 Depth 5 m	Station 8 Depth 5 m
Percent of total volume in the size range 1.59-6.35 µm	75	82	86	87	95	65	70
Predominant particle size range (µm)	4.00-6.35	1.59-2.52	2.00-3.17	2.0-6.35	4.00-8.00	4.00-8.00	3.17-6.35
Percent of total volume	33	49	53	76	27	31	40
Total population	488,466	429,948	535,526	496,446	389,716	402,079	527,988
Suspended particle load ($mg \cdot L^{-1}$)	5.05	5.47	4.48	5.15	3.72	3.65	5.37

Figure 3.4 Particle size of suspended particulate material from Main Channel, February 1986, as determined by light scattering, Coulter Counter and Sedigraph analysis



3.2.2.3 Comparison of Methods

The data for 1985 and 1986 are in general agreement, with both Coulter Counter and HIAC/ROYCO light scattering methods indicating a maximum in size distribution in the range of 3 - 6 micrometres. The general agreement of the methods was confirmed by analysis of stored samples in 1986 (Figure 3.4).

The Sedigraph data give quite different results than are obtained with an analysis of suspended solids. It is unclear why there should be such a large difference. The results from the Sedigraph may reflect the method of sample treatment (i.e. freeze dried sample, resuspension). Results for the other methods require no pretreatment and therefore are more indicative of in situ conditions. The larger particle size may be indicative of particle aggregates which are broken down in the sample treatment for Sedigraph analysis into smaller "base" particles. Further comparisons are warranted to try to relate the more standard sedimentation type Sedigraph analysis with results for "in situ" conditions. From the standpoint of sedimentation processes and uptake of environmentally important chemicals, the available surface area and the "in situ" particle size is of greatest importance. Non-destructive testing procedures, such as a light scattering based measurement system are preferable for estimations of "in situ" conditions. The effect of storage of the sample appears to be slight, at least in describing the size distribution of the samples examined. Analysis of samples immediately after collection would be preferable, but if not possible, storage for hours or weeks does not appear to yield significantly different results.

3.2.3 Particulate Organic Carbon and Nitrogen

Particulate organic carbon and nitrogen (POC and PON) results for April 1985 and February 1986 are given in Table 3.6. An ANOVA for POC indicated no significant differences (alpha = 0.05) between channels, depths or locations across channel but a difference between years in the East Channel (mean POC in 1985: 385 $\mu g \cdot L^{-1}$ and in 1986: 252 $\mu g \cdot L^{-1}$). Since the SPM concentrations in the East Channel in 1985 and 1986 were similar, the differences in POC may reflect a real change or seasonal variation. However, as the 1985 samples were kept for over a year before analysis, the difference may also be an artifact of storage.

The organic content of these samples was calculated using mean SPM values for the respective channel at that time and the results are given in Table 3.7. These values range from levels that are similar to Beaufort Sea nearshore silt/clay

Table 3.6.

Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON) in Suspended Particulate Material

Sample*	Date	Channel	Hole	Depth (m)	POC (µg.L-1)	PON (µg.L-1)	C:N
4-1-2a	18/04/85	East	4	6	352	40.8	8.6
4-1-2b	18/04/85	East	4	6	428	39.6	10.8
5-1-1a	20/04/85	East	5	4	455	41.9	10.9
5-1-1b	20/04/85	East	5	4	402	40.2	10.0
5-2-1a	20/04/85	East	5	6	373	35.5	10.5
5-2-1b	20/04/85	East	5	6	405	41.4	9.8
8-1a	20/04/85	East	8	5	452	94.4	10.2
8-1b	20/04/85	East	8	5	398	38.9	10.2
1985 mean					385	40.3	10.1
NW-2-1	01/02/86	Middle	C	4	165	13.6	12.1
NW-2-2	01/02/86	Middle	C	10	347	19.5	17.8
NW-2-3	01/02/86	Middle	W	10	122	10.5	11.6
NW-2-4	01/02/86	Middle	E	10	176	14.2	12.4
NW-2-5	04/02/86	Reindeer	C	4	223	15.1	17.8
NW-2-6	04/02/86	Reindeer	C	10	179	14.7	12.2
NW-2-7	04/02/86	Reindeer	W	8	267	13.7	19.5
NW-2-8	04/02/86	Reindeer	E	8	313	10.2	30.7
NW-2-9	06/02/86	Main	E	10	343	11.1	30.9
NW-2-10	06/02/86	Main	W	10	214	7.8	27.4
NW-2-11	06/02/86	Main	C	4	323	9.4	34.9

* a and b denote replicate samples.

....cont'd.

Table 3.6, cont'd.

Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON)
in Suspended Particulate Material

Sample	Date	Channel	Hole	Depth (m)	POC (µg.L-1)	PON (µg.L-1)	C:N
NW-2-12	06/02/86	Main	C	10	262	7.5	34.9
NW-2-13	07/02/86	East	C	13	184	11.4	16.1
NW-2-14	07/02/86	East	C	8	296	19.5	15.2
NW-2-15	07/02/86	East	C	3	200	8.4	23.8
NW-2-16	08/02/86	East	C	3	349	17.3	20.2
NW-2-1	07/02/86	East	W	4	294	28.9	10.2
NW-2-18	07/02/86	East	E	5	274	33.1	8.3
1986 mean					252	14.8	19.7

Table 3.7.

Summary of Organic Carbon in Suspended Sediment

Location and Date	Sample* I.D.		% Organic Carbon	
East Channel	4-1-2	a	7.4	
April 1985		b	9.1	
	5-1-1	a	9.7	
		b	8.5	
	5-2-1	a	7.9	Mean 1985:
		b	8.6	8.7%, s=0.94%
				n=8
	8-1	a	9.6	
		b	8.4	
Middle Channel	NW-2	-1	3.6	
February 1986		-2	7.6	
		-3	2.7	
		-4	3.8	
Reindeer Channel		-5	4.5	
February 1986		-6	3.6	
		-7	5.4	
		-8	6.4	
Main Channel		-9	5.2	Mean 1986:
February 1986		-10	3.2	4.8%, s=1.3%
		-11	4.9	n=18
East Channel		-12	4.0	
February 1986		-13	3.6	
		-14	5.7	
		-15	3.9	
		-16	6.8	
		-17	5.7	
		-18	5.3	

* a and b denote replicate samples.

surficial sediments to values several times higher. The Mackenzie River was a source of total organic carbon to the waters near Issungnak in winter sampling in 1982 (Erickson et al., 1983). These results indicate that river derived particulates would be a major source of the total organic carbon found in winter river diluted shelf water.

The C:N ratios of the particulate material are also typical of a silt/clay marine sediment except for a few higher values in the Main Channel (C:N >30). The higher C:N ratio is more typical of terrestrial plant matter where C:N ratios may be 100 or more; marine plants have C:N ratios closer to 10.

3.3 Nutrients (Reactive Silicate, Orthophosphate, Nitrate)

Nutrient results are summarized in Table 3.8 for the East Channel, April 1985 and in Table 3.9 for all four channels sampled in February 1986. There were no significant differences between concentrations of all nutrients observed in 1985 and 1986 in the East Channel. The data also indicate there were no significant differences (alpha = 0.05) between the main channels of the Delta for silicate. There were significant differences in nitrate and phosphate concentrations however. Lowest concentrations of both nitrate and phosphate were in the Middle Channel. However, although means were significantly different, the Middle Channel mean for nitrate was only 4% lower than East Channel results. Mean phosphate concentrations were about 40% lower than the maximum mean in other channels or 0.04 $\mu mol \cdot m^{-3}$.

No significant differences were found with respect to depth or location for nitrate or silicate in the East Channel. Phosphate concentrations were not significantly different with depth but significant although slight in magnitude, differences were found in cross-channel phosphate concentrations. Time series measurements indicated no significant (alpha = 0.05) differences over the 15 h time period for any nutrient.

The data suggest that nutrient concentrations are relatively constant throughout the winter and vary little from year to year or from channel to channel. Mean values for each nutrient are given below where they are compared with winter concentrations on the Beaufort Sea Shelf observed near Esso's Issungnak artificial island site in 1981 and 1982.

Table 3.8.

Dissolved Nutrients in the East Channel, April 1985
($mmol \cdot m^{-3}$)

Station	Depth (m)	Replicate	Nitrate	Phosphate	Silicate
5	5	1	9.6	0.08	59.8
		2	9.4	0.11	60.0
		3	9.7	0.10	61.0
		mean	9.6	0.10	60.3
		Std. dev.	0.1	0.01	0.6
5	8	1	9.6	0.12	65.3
		2	9.7	0.11	59.1
		3	9.6	0.11	59.7
		mean	9.6	0.11	61.3
		Std. dev.	0.1	0.01	3.4
6	5	1	9.6	0.06	58.9
		2	9.6	0.06	65.5
		3	9.4	0.07	57.7
		mean	9.5	0.06	60.7
		Std. dev.	0.1	0.01	4.2
8	5	1	8.9	0.11	58.8
		2	9.6	0.08	60.4
		3	9.6	0.07	61.0
		mean	9.4	0.09	60.1
		Std. dev.	0.4	0.03	1.1
2	7	1	9.6	0.08	55.7
		2	9.6	0.12	53.9
		3	9.6	0.09	62.5
		mean	9.6	0.10	57.4
		Std. dev.	-	0.02	4.5
4	5	1	9.6	0.08	59.5
		2	9.5	0.10	59.4
		3	9.5	0.10	59.4
		mean	9.6	0.08	60.3
		Std. dev.	0.1	0.02	1.4
5	2	1	9.6	0.11	59.2
		2	9.6	0.12	60.4
		3	9.6	0.10	59.0
		mean	9.6	0.11	59.5
		Std. dev.	-	0.01	0.8
Mean All Sites (± 1 Std. deviation)			9.5 0.2	0.09 0.02	59.8 2.6

Table 3.9

Dissolved Nutrients, Main, East, Reindeer and Middle Channels

February 1 - 8, 1986
($mmol \cdot m^{-3}$)

Channel	Position E = East W = West C = Centre	Depth (m)	Nitrate (nitrite)	Silicate	Phosphate
Main	C	5	9.2	67.0	0.08
			9.3	56.0	0.07
		10	9.2	59.3	0.03
			9.3	60.4	0.08
		20	9.4	63.1	0.07
			9.2	61.7	0.08
	W	10	9.4	60.7	0.11
			9.2	64.2	0.10
	E	8	9.3	59.0	0.09
			9.3	63.4	0.12
	Mean ± 1 Std. dev.		9.3 ±0.1	61.5 ±3.1	0.08 ±0.02
Middle	C	10	9.0	59.7	0.05
			9.1	58.3	0.06
		16	9.0	61.7	0.05
			9.0	*	0.06
	W	8	9.1	59.1	0.06
			9.0	*	0.07
	E	8	9.0	60.2	0.09
			9.0	59.4	0.06
	Mean ± 1 Std. dev.		9.0 ±0.05	59.7 ±1.2	0.06 ±0.01
Reindeer	C	4	9.1	60.0	0.08
			9.1	59.4	0.09
		10	9.2	59.4	0.11
			9.1	*	0.09
	W	8	9.2	57.5	0.11
			9.1	58.7	0.08
	E	8	9.2	59.5	0.06
			9.2	*	0.06
	Mean ± 1 Std. dev.		9.2 ±0.05	59.1 ±0.9	0.09 ±0.02

Table 3.9, cont'd

Dissolved Nutrients, Main, East, Reindeer and Middle Channels

February 1 - 8, 1986

Channel	Position E = East W = West C = Centre (Time)	Depth (m)	Nitrate (nitrite)	Silicate	Phosphate
East	C	3	9.3	60.0	0.10
	(1400)		9.3	57.9	0.11
		8	9.3	60.0	0.10
			9.4	*	0.11
	W	5	9.5	60.1	0.07
			9.6	*	0.07
			9.6	58.1	0.06
	E	5	9.3	63.6	0.12
			9.3	57.5	0.14
			9.3	61.2	0.12
	C	3	9.3	61.0	0.09
	(2300)		9.3	60.4	0.09
	C	3	9.3	57.9	0.09
	(0845)		9.3	60.4	0.09
	Mean ± 1 Std. dev.		9.4 ±0.1	59.8 ±1.8	0.10 ±0.0

* Sample vials cracked - contamination suspected.

	Nitrate ($\mu mol.m^{-3}$)	Soluble Reactive Phosphate ($\mu mol.m^{-3}$)	Reactive Silicate ($\mu mol.m^{-3}$)
Issungnak 1981, 1982 s = 32 - 33% (Erickson et al., 1983)	8 - 10.0	1.3 - 1.4	22 - 24
Mean values this study	9.3	0.09	60.0

The Mackenzie River in the winter is a source of silicate. Phosphate concentrations are more than an order of magnitude higher on the shelf, however, while nitrate concentrations appear to be similar in the river and shelf waters.

3.4 Major Ions

Results for major ion concentrations from the East Channel in April 1985 and for the Main, East, Middle and Reindeer Channels in February 1986 are given in Tables 3.10 and 3.11. Across channel and depth variations indicate that in both years and in all channels, the river was relatively well mixed. ANOVA of the 1986 data indicated that there were no significant (alpha = 0.05) differences in concentrations between channels, and no significant differences in 15 h time series measurements (Table 3.12).

There were differences however between 1985 and 1986 data for some metals and anions. As noted in the Methods Section (2.2.2), aluminum values from April 1985 are thought to be in error: the Al data in 1986 are consistent with limited winter data for extractable Al levels in the Mackenzie River above Arctic Red River (Inland Waters Directorate, 1980) and waters from the Great Bear Lake Basin (<3.7 $mmol \cdot m^{-3}$) Unlike other major cations and anions, Al concentrations appear to decrease in winter low flow conditions. Sulphate concentrations were almost 50% higher in 1986 compared to 1985, while both Mg and Ca concentrations were slightly higher. The higher sulphate, Mg and Ca concentrations in 1986 may be a result of analytical bias although analysis of reference materials both years for sulphate and Mg did not indicate a calibration error. Ca levels measured in SLRS-1 were slightly high so that 1986 Ca concentrations may not be significantly different than 1985 concentrations. Extrapolation of the downstream trend in sulphate concentrations past Arctic Red River would give a sulphate concentration of between 35 - 40 $mg \cdot L^{-1}$

Table 3.10.

Concentration of Major Ions in the East Channel,
April 1985

Station	Depth (m)	Replicate	Al [a]	Fe	K	Na*	Mg*	Ca*	Mn	Ba	Cl*	F	SO_4*
5	5	1	7.8	2.5	23	.43	.34	.90	.11	.41	.49	3.2	.30
		2	7.8	2.4	28	.46	.37	.92	.11	.41	.49	2.6	.30
		3	7.8	2.5	31	.48	.38	.93	.11	.41	.48	1.6	.30
		mean	7.8	2.5	27	.46	.36	.91	.11	.41	.49	2.5	.30
		Std. dev.	-	0.1	4	.03	.02	.02	-	-	.004	0.8	.002
5	8	1	8.2	2.5	28	.49	.38	.93	.11	.42	.48	1.6	.30
		2	8.5	2.5	31	.49	.38	.94	.11	.42	.48	2.6	.30
		3	8.2	2.4	28	.46	.37	.92	.11	.42	.49	1.6	.30
		mean	8.3	2.5	29	.48	.38	.93	.11	.42	.48	1.9	.30
		Std. dev.	0.2	0.1	2	.02	.006	.01	-	-	.008	0.6	.002
6	5	1	7.8	2.5	28	.46	.37	.92	.11	.41	.47	1.1	.30
		2	8.2	2.5	31	.47	.37	.92	.11	.41	.47	1.6	.30
		3	8.2	2.5	31	.51	.39	.96	.11	.41	.48	2.1	.31
		mean	8.1	2.5	30	.48	.37	.93	.11	.41	.47	1.6	.30
		Std. dev.	0.2	-	2	.03	.01	.02	-	-	.003	0.5	.001
8	5	1	6.7	2.6	26 [b]	.41	.33	.90 [b]	.11	.39	.47	1.6	.30
		2	7.8	2.5	15 [b]	.46	.38	.78 [b]	.11	.39	.47	2.6	.30
		3	-	-	-	-	-	-	-	-	.47	1.6	.30
		mean	7.3	2.6	-	.44	.36	-	.11	.39	.47	1.9	.30
		Std. dev.	-	-	-	-	-	-	-	-	.002	0.6	.002
2	7	1	7.8	2.1	33	.52	.39	.97	.07	.44	.49	4.2	.30
		2	7.4	2.3	31	.53	.39	.97	.07	.44	.49	4.2	.31
		3	8.2	2.2	33	.53	.40	.97	.11	.42	.49	4.2	.30
		mean	7.8	2.2	32	.52	.40	.97	.08	.43	.49	4.2	.30
		Std. dev.	0.4	0.1	1	.003	.001	.001	.02	.01	-	-	.002
4	5	1	7.8	2.4	33	.47	.38	.94	.11	.42	.49	4.2	.30
		2	7.8	2.5	31	.48	.38	.94	.11	.42	.49	4.2	.30
		3	7.8	2.5	31	.48	.38	.94	.11	.42	.49	4.2	.30
		mean	7.8	2.5	32	.48	.38	.94	.11	.42	.49	4.2	.30
		Std. dev.	-	0.1	1	.005	.002	-	-	-	-	-	-
5	2	1	7.8	2.5	31	.44	.36	.93	.11	.42	.50	4.2	.31
		2	7.4	2.6	26	.44	.35	.93	.11	.42	.51	4.2	.30
		3	7.4	2.5	31	.53	.40	.96	.11	.44	.50	3.7	.30
		mean	7.5	2.5	29	.47	.37	.94	.11	.43	.50	4.0	.30
		Std. dev.	0.2	0.1	3	.05	.03	.02	-	.01	.003	0.3	.002
	Mean all sites		7.5	2.4	30	0.48	0.37	0.94	0.11	0.42	0.49	2.9	0.30
	(±1 Std. deviation)		1.6	0.1	3	0.03	0.02	0.03	0.00	0.02	0.02	1.2	0.01

Concentrations in $mmol \cdot m^{-3}$ except $mol \cdot m^{-3}$ for metals and anions denoted with *

a - All Al results are thought to be too high due to a calibration/blank error (see Section 2.2.2).

b - Omitted from mean.

Table 3.11.

Total Major Ions, Main, East, Reindeer and Middle Channels, Mackenzie River, February 1 - 8, 1986

Channel	Location	Depth (m)	Al	Na*	K	Ca*	Mg*	Ba	Fe	Mn	Cl*	F	SO_4*
Main	C	5	2.0	0.53	31	1.00	0.43	0.45	2.1	0.09	0.48	2.6	0.44
			2.1	0.50	28	1.01	0.44	0.46	3.0	0.07	0.48	2.1	0.44
		10	1.7	0.50	26	1.01	0.43	0.45	1.8	0.07	0.48	2.1	0.44
			1.5	0.51	28	1.02	0.43	0.46	1.8	0.06	0.48	2.1	0.44
		20	1.5	0.50	28	1.00	0.44	0.46	2.4	0.08	0.48	3.2	0.44
			1.6	0.50	28	1.01	0.43	0.46	2.1	0.07	0.48	3.7	0.44
		26	1.6	0.52	31	1.03	0.43	0.45	2.0	0.06	0.48	3.7	0.44
			1.5	0.50	28	1.00	0.43	0.45	1.8	0.06	0.48	3.2	0.43
	E	8	1.5	0.51	31	0.97	0.43	0.45	1.8	0.07	0.48	4.2	0.44
			1.5	0.50	28	1.00	0.43	0.45	1.8	0.08	0.48	3.2	0.44
	W	10	1.8	0.50	28	0.98	0.44	0.46	1.8	0.06	0.48	3.2	0.44
			1.5	0.52	28	1.01	0.43	0.45	1.8	0.06	0.48	3.2	0.41
	Mean		1.7	0.51	27	1.00	0.43	0.45	2.0	0.07	0.48	2.9	0.44
	±1 Standard deviation		0.2	0.01	6	0.02	0.01	0.01	0.3	0.01	±0.00	1.1	0.01

Concentrations in mmol m^{-3} except mol m^{-3} where noted with *

Table 3.11, cont'd.

Total Major Ions, Main, East, Reindeer and Middle Channels, Mackenzie River, February 1 - 8, 1986

Channel	Location	Depth (m)	Al	Na*	K	Ca*	Mg*	Ba	Fe	Mn	Cl*	F	SO_4*
East	C	3	1.7	0.50	28	1.01	0.42	0.44	1.8	0.05	0.48	2.6	0.44
			1.5	0.50	28	1.01	0.41	0.43	1.8	0.05	0.48	2.1	0.44
		8	1.7	0.50	28	0.96	0.42	0.43	1.8	0.07	0.48	2.1	0.44
			1.6	0.51	28	0.98	0.42	0.44	2.0	0.08	0.48	3.2	0.41
	E	5	1.5	0.52	26	1.03	0.42	0.43	1.8	0.05	0.45	2.1	0.43
			1.5	0.51	28	0.98	0.42	0.42	2.0	0.08	0.48	2.1	0.45
	W	5	1.8	0.49	28	1.02	0.43	0.44	1.8	0.06	0.41	2.6	0.45
			1.5	0.52	28	0.98	0.41	0.43	1.9	0.05	0.48	3.2	0.41
	Mean		1.6	0.51	28	1.00	0.42	0.43	1.9	0.06	0.47	2.5	0.43
	± 1 Standard deviation		0.1	0.01	1	0.02	0.01	0.01	0.2	0.02	0.02	0.5	0.02

Concentrations in $mmol \cdot m^{-3}$ except $mol \cdot m^{-3}$ where noted with *

Table 3.11, cont'd.

Total Major Ions, Main, East, Reindeer and Middle Channels, Mackenzie River, February 1 - 8, 1986

Channel	Location	Depth (m)	Al	Na*	K	Ca*	Mg*	Ba	Fe	Mn	Cl*	F	SO_4*
Reindeer	C	4	1.4	0.51	31	1.00	0.44	0.45	1.8	0.08	0.45	3.2	0.44
			1.5	0.50	31	0.97	0.43	0.45	1.8	0.06	0.41	3.2	0.44
		10	1.5	0.50	28	0.98	0.44	0.45	2.1	0.06	0.48	3.7	0.43
			1.6	0.50	28	0.98	0.44	0.46	2.4	0.07	0.48	2.6	0.43
		18	1.5	0.51	26	0.98	0.43	0.45	1.8	0.06	0.45	2.1	0.43
			1.5	0.50	28	0.97	0.43	0.44	1.8	0.06	0.48	2.6	0.42
	E	8	1.5	0.52	28	1.01	0.43	0.44	2.1	0.06	0.41	2.6	0.44
			1.5	0.50	28	1.00	0.43	0.46	1.8	0.07	0.48	2.1	0.41
	W	8	2.0	0.50	28	1.03	0.43	0.45	1.8	0.08	0.48	1.8	0.45
			1.5	0.50	26	1.00	0.43	0.45	2.1	0.07	0.48	2.1	0.42
	Mean		1.5	0.50	0.28	0.99	0.43	0.45	2.0	0.07	0.46	2.6	0.43
	± 1 Standard deviation		0.2	0.01	0.02	0.02	0.01	0.01	0.2	0.01	0.02	0.6	0.01

Concentrations in $mmol \cdot m^{-3}$ except $mol \cdot m^{-3}$ where noted with *

Table 3.11, cont'd.

Total Major Ions, Main, East, Reindeer and Middle Channels, Mackenzie River, February 1 - 8, 1986

Channel	Location	Depth (m)	Al	Na*	K	Ca*	Mg*	Ba	Fe	Mn	Cl*	F	SO_4*
Middle	C	5	1.5	0.50	28	0.97	0.42	0.44	1.8	0.05	0.48	3.7	0.43
			1.7	0.49	28	0.98	0.42	0.43	1.9	0.07	0.45	2.6	0.44
		10	1.7	0.51	31	0.97	0.42	0.44	1.9	0.05	0.48	3.2	0.44
			1.5	0.52	26	0.99	0.41	0.44	1.7	0.07	0.41	2.1	0.45
		16	1.4	0.50	28	1.00	0.41	0.43	2.0	0.06	0.48	3.2	0.41
			1.5	0.49	28	1.01	0.42	0.42	1.9	0.05	0.48	2.6	0.43
	E	8	1.8	0.52	28	1.02	0.42	0.44	1.8	0.08	0.45	2.6	0.44
			2.1	0.50	28	0.99	0.42	0.44	1.8	0.06	0.48	2.1	0.44
	W	8	1.6	0.50	28	1.01	0.42	0.44	1.8	0.05	0.41	2.6	0.41
			1.5	0.49	26	1.01	.0.41	0.44	1.8	0.05	0.48	2.1	0.45
	Mean		1.6	0.50	28	0.99	0.42	0.44	1.8	0.06	0.46	2.7	0.43
	± 1 Standard deviation		0.2	0.01	1	0.01	0.01	0.01	0.1	0.01	0.02	0.4	0.02

Concentrations in $mmol \cdot m^{-3}$ except $mol \cdot m^{-3}$ where noted with *

Table 3.12.

Time Series Measurements of Major Ions, East Channel, Centre, 3 m,
February 8, 1986

Channel	Location	Time	Al	Na*	K	Ca*	Mg*	Ba	Fe	Mn	Cl*	F	SO_4*
Time Series													
East	Centre, 3 m	1400	1.7	0.50	28	1.01	0.42	0.44	1.8	0.05	0.48	2.6	0.44
			1.5	0.50	28	1.01	0.41	0.43	1.8	0.05	0.48	2.1	0.44
		2300	1.4	0.51	28	0.99	0.42	0.43	1.8	0.07	0.48	3.2	0.41
			1.5	0.49	26	1.00	0.41	0.43	2.0	0.05	0.45	2.1	0.43
		0845	1.5	0.49	31	0.99	0.43	0.43	1.9	0.04	0.45	2.1	0.45
			1.5	0.52	28	1.01	0.42	0.43	1.8	0.05	0.48	1.6	0.44
	Mean		1.5	0.50	28	1.00	0.42	0.43	1.8	0.05	0.47	2.3	0.44
	± 1 Standard deviation		0.1	0.01	1	0.01	0.01	0.01	0.1	0.01	0.02	0.5	0.01

Concentrations in $mmol \cdot m^{-3}$ except $mol \cdot m^{-3}$ where noted with *

(Mackenzie River Basin Committee, 1981). The 1986 data are slightly higher than this range which might be expected with the low winter flows. The 1985 data are below this range.

Both Fe and Mn concentrations were slightly lower in 1986. The manganese concentrations in both years were near the detection limit for Mn by ICP and the differences may not be significant. Iron concentrations were about 20% lower in 1986.

Concentrations of major cations and anions are higher than summer historical values (Mackenzie River Basin Committee, 1981) and those reported by Levinson et al. (1969) for the February-April period at Norman Wells. The increase in major cations in winter reflects the lower flows. Levinson et al. (1969) estimated that in winter the Great Slave and Great Bear Lakes may contribute as much as 75 - 80% of the total flow. Ground water likely also contributes a much greater relative amount of water at this time of year.

3.4.1 Dissolved vs Particulate

Direct measurement of major ions in particulate material was not made. Both filtered and unfiltered samples were analyzed however. Results for unfiltered samples should give a measure of total cations while filtered samples should yield results for dissolved species.

Comparison of data for filtered vs unfiltered samples indicates that most cations are predominantely in the dissolved phase. However for Fe, Mn and Al, a significant proportion of the total concentration is particulate. Table 3.13 suggests that over 80% of Mn is particulate while about 30% of Al is associated with particulates. The iron ratio of filtered to unfiltered samples varied considerably. This may be a function of storage time between collection and filtration. At least 70% of total iron appears to be particulate although in many samples the ratios suggest that >98% is associated with particulates.

3.5 Trace Metals in Particulates

The results of trace metal analyses of particulates collected in 1985 by filtration and in 1986 by centrifugation are summarized in Table 3.14. There is

Table 3.13.

Major Cations
Dissolved and Total Concentrations
$mmol.m^{-3}$

Metal		Filtered	Unfiltered	Unfiltered/ Filtered	Mean
Al	a	5.2*	7.4*	1.4*	
	b	5.6*	7.8*	1.3*	1.31
	c	1.1	1.6	1.4	
	d	1.8	2.1	1.1	
Fe	a	.09	2.56	28.4	
	b	< .05	2.45	>49	variable
	c	0.55	1.75	3.2	3 - >49
	d	28.1	28.1	1.0	
K	a	33.2	28.1	0.84	
	b	30.7	28.1	0.92	0.94
	c	28.1	28.1	1.00	
	d	28.1	28.1	1.00	
Na	a	535	470	0.88	
	b	457	370	0.81	0.93
	c	531	518	1.03	
	d	539	531	0.99	
Mg	a	406	369	0.91	
	b	404	362	0.90	0.94
	c	448	432	0.96	
	d	436	436	1.00	
Ca	a	983	940	0.96	
	b	973	913	0.94	0.97
	c	1013	1013	1.00	
	d	1023	1008	0.99	
Mn	a	< 0.02	0.11		
	b	< 0.02	0.11		>6
	c	< 0.02	0.09		
	d	< 0.02	0.09		
Ba	a	0.45	0.42	0.93	
	b	0.43	0.41	0.95	1.06
	c	0.38	0.46	1.21	
	d	0.39	0.45	1.15	

a - East Channel, Station 5 2 m, April 1985
b - East Channel, Station 5 5 m, April 1985
c - East Channel, Centre, 3 m, February 1986,
d - Main Channel, Centre 5 m, February 1986
* 1985 Al values are thought to be in error due to calibration/blank problems.

Table 3.14

Concentration of Trace Metals in Suspended Particulates
(nmol·g^{-1} except where noted)

	Cu	Cd	Pb[a]	Zn	Ni	Cr	V	As	Hg
1) East Channel, Site 5, 5 m									
April 1985 (mean of 3)	706	5.1	89.3	2750	520	2130	2748	b	0.99
East Channel, Site 5, 2 m									
April 1985 (mean of 3)	680	5.5	106	3010	528	2230	2510	b	1.10
Mean:	693 ± 20	5.3 ±0.4	97.8 ±21.4	2880 ±268	524 ±85	2180 ±110	2630 ±320	-	1.05±0.10
Average SPM: g·m^{-3}	4.78	4.78	4.78	4.78	4.78	4.78	4.78	-	4.78
Total Metal per m^3 = A	3310	25.33	468	13800	2550	10400	12566	-	5.02
Flux (A x 1100)[c]: mmol·m^{-3}·sec^{-1}	3.64	0.028	0.72	15.2	2.8	11.4	13.8	-	0.005
2) Main Channel, Sedisamp	1289	5.2	139	2620	698	2250	3160	107	0.45
8 m, February 1986	1134	5.0	92.8	2937	630	2115	3298	95	0.49
Mean:	1212	5.1	116	2779	664	2182	3229	101	0.47
Average SPM: g·m^{-3}	6.53	6.53	6.53	6.53	6.53	6.53	6.53	6.53	6.53
Total Metal per m^3 = A	7911	33.3	760	18143	4336	14248	21085	659	3.07
Flux (A x 2800)[c]: mmol·m^{-3}·sec^{-1}	22.2	0.093	2.98	50.8	12.14	39.90	59.04	1.85	0.009
3) East Channel, Sedisamp	994	6.6	75.0	3136	724	2365	3533	80	0.43
5 m, February 1986	761	5.8	96.4	2448	637	2518	2436	90	0.46
Mean:	878	6.2	85.7	2792	681	2452	2985	85	0.45
Average SPM: g·m^{-3}	5.15	5.15	5.15	5.15	5.15	5.15	5.15	5.15	5.15
Total Metal/ per ^{3} = A	4522	31.93	441	14379	3507	12626	15370	438	2.32
Flux (A x 1100)[c]: mmol·m^{-3}·sec^{-1}	4.97	0.035	0.68	15.8	5.8	13.9	16.9	0.48	0.002
4) Reindeer Channel, Sedisamp	1010	6.14	111	3365	647	2230	3632	80	0.46
8 m; February 1986	1025	5.96	136	3518	613	2173	2807	107	0.50
Mean:	1018	6.05	124	3442	630	2201	3220	93	0.48
Average SPM: g·m^{-3}	4.89	4.89	4.89	4.89	4.89	4.89	4.89	4.89	4.89
Total Metal per m^3 = A	4978	29.58	604	16831	3081	10765	15746	455	2.35
Flux (A x 990)[c]: mmol·m^{-3}·sec^{-1}	4.93	0.029	0.84	16.7	3.05	10.6	15.6	0.45	0.002
5) Middle Channel, Sedisamp	1025	5.43	175	1912	647	2307	3043	107	0.47
8 m; February 1986	97.9	5.60	132	2200	1073	2250	2787	174	0.51
Mean:	1002	5.51	154	2056	860	2279	2915	141	0.49
Average SPM: g/m^3	4.58	4.58	4.58	4.58	4.58	4.58	4.58	4.58	4.58
Total Metal per m^3 = A	4589	25.24	704	9416	3939	10436	13351	646	2.24
Flux (A x 690)[c]: mmol·m^{-3}·sec^{-1}	3.17	0.017	0.68	6.50	2.7	7.2	9.2	0.45	0.002

a - Flux calculations for lead were corrected by multiplication x 1.4 due to the 60% efficiency of recovery observed in analyses of certified reference materials.
b - Insufficient material for analyses.
c - Flux is given as total metal per m^3 x measured discharge (m^3·sec^{-1}).
All values are a mean of 3 subsamples except where noted.

general agreement in concentrations between years and between channels. There are differences for particular metals but no systematic trends.

Mercury concentrations from filtered East Channel samples in 1985 are about twice the concentrations in February 1986. In 1986, mean Hg concentrations in each channel were within 0.05 $mol \cdot m^{-3}$ of each other.

Copper concentrations were quite variable between channels and in all instances higher than results for the East Channel in 1985 (Main Channel Cu concentrations were almost twice 1985 concentrations in the East Channel). Nickel particulate concentrations were more uniform than for Cu between channels and about 25% higher than East Channel results in 1985.

The concentrations of metals in particulates from different channels are compared with concentrations in surficial sediments of the Beaufort Sea Shelf in Table 3.15. The shelf data are from an EPS Yellowknife data compilation (Hoff and Thomas, 1986) for the 10-20 m depth range and include only data with a 3 or 4 quality rating. Concentrations of all metals in winter river particulates collected by filtration or centrifugation are higher than concentrations in shelf sediments. Either winter particulates from the river lose metals before or after deposition on the shelf or summer particulates have lower trace metal concentrations and dilute the concentration of particulates from the winter months.

Higher concentrations may also be a function of particle size. Trace metal concentrations in sediments are known to increase with decreasing particle size. Shelf sediment concentrations are for bulk sediment and are not corrected for particle size. Some coarse silt and even sand may be present. Winter river particulates, however, have particles less than 10 µm and in the Sedisamp samples, mainly less than 1.0 µm.

3.6 Trace Metals in Water

Trace metal results from the East Channel, April 1985 are summarized in Table 3.16. Results for February 1986 sampling in all four channels are given in Table 3.17. ANOVA indicated no significant (alpha = 0.05) differences for any metals in time series measurements in 1986 or in 1985 with respect to depth. There were no significant differences in concentrations of Cu, Cr, As or Hg between channels (alpha = 0.05). Differences were significant for the remaining metals but in all cases the magnitude of between channel variations was less than 20%. Given the relatively small contribution of the winter discharge in terms of the annual total,

Table 3.15.

Comparison of Trace Metal Concentrations in Winter Mackenzie River Particulates and Concentrations in Surficial Beaufort Sea Shelf Sediments (in $\mu mol \cdot kg^{-1}$)

Metal	Beaufort Sea Shelf*	East Channel 1985	East Channel 1986	Main Channel 1986	Reindeer Channel 1986	Middle Channel 1986
Cu	354 ± 162	693	878	1212	1018	1025
Cd	2.58 ± 1.6	5.3	6.2	5.1	6.1	5.5
Pb	65.7 ± 23.5	137	120	163	173	215
Zn	1637 ± 750	2880	2792	2779	3442	2056.
Ni	572 ± 272	524	1030	664	630	860
Cr	1288 ± 456	2180	2452	2182	2201	2279
V	2002 ± 1256	2630	2985	3229	3220	2915
As	130 ± 55	-	85	101	93	141
Hg	0.35 ± 0.15	1.05	0.35	0.47	0.48	0.49

* 10 - 20 m, data quality rating 3 or 4. EPS Yellowknife, data compilation mean ± 1 standard deviation (EPS Yellowknife, 1986).

Table 3.16.

Trace Metal Concentrations in the East Channel, April 16-19, 1985
(Concentrations in $\mu mol \cdot m^{-3}$)

Station	Depth	Description	Replicate	As	Cd	Cu	Cr	Hg	Ni	Pb	V	Zn
5	2	unfiltered	1	4.0	-	-	-	0.04	-	-	-	-
			2	4.0	0.09	19.7	5	0.03	63.8	4.1	78.9	18.5
			3	2.7	0.12	20.6	6.5	0.04	67.7	4.8	84.6	24.9
			mean	3.6	0.11	20.2	5.8	0.04	65.8	4.5	81.7	21.7
			Std. dev.	0.8	NC	NC	NC	0.01	NC	NC	NC	NC
	2	filtered	1	4.0	0.20	a	6.5	0.03	80.9	3.9	84.6	8.1
			2	4.0	0.13	a	3.8	0.03	82.8	4.0	81.7	7.6
			3	4.0	0.16	a	4.4	0.04	78.7	3.5	82.4	7.6
			mean	4.0	0.16	NC	4.9	0.03	80.8	3.8	82.9	7.8
			Std. dev.	NC	0.03	NC	1.4	0.01	2.1	0.3	1.5	0.3
	5	unfiltered	1	2.7	-	-	-	0.04	-	-	-	-
			2	4.0	0.10	19.7	5.8	0.03	67.0	3.7	67.5	22.2
			3	4.0	0.11	20.9	6.5	0.04	85.7	4.4	67.5	21.7
			mean	3.6	0.11	20.3	6.2	0.04	62.9	4.1	67.5	22.0
			Std. dev.	0.8	NC	NC	NC	0.01	NC	NC	NC	NC
	5	filtered	1	4.0	0.13	a	5.8	0.03	81.8	4.5	a	10.7
			2	4.0	0.11	a	5.2	0.05	82.8	4.8	a	11.6
			3	4.0	0.10	a	5.2	0.04	82.3	4.6	a	10.7
			mean	4.0	0.11	NC	5.4	0.04	82.3	4.6	NC	11.0
			Std. dev.	-	0.02	NC	0.3	0.01	0.5	0.2	NC	0.5
5	8	unfiltered	1	2.7				0.01	-	-	-	-
			2	4.0	0.11	18.3	9.6*	0.03	83.0	4.1	73.2	21.7
			3	4.0	0.12	21.2	6.5	0.02	59.9	5.0	73.2	21.1
			mean	3.6	0.12	19.8	8.1	0.02	72.0	4.6	73.2	21.4
			Std. dev.	0.8	NC	NC	NC	0.01	NC	NC	NC	NC

* Omitted from mean - contamination suspected.
a Filtered values were approximately 50% higher than unfiltered concentrations.
\- Indicates no data.
NC Indicates not computed.

Table 3.16, cont'd.

Trace Metal Concentrations in the East Channel, April 16-19, 1985
(Concentrations in $\mu mol \cdot m^{-3}$)

Station	Depth	Description	Replicate	As	Cd	Cu	Cr	Hg	Ni	Pb	V	Zn
2	7	unfiltered	1	-	-	-	-	0.03	-	-	-	-
			2	4.0	0.12	20.6	5.8	0.01	59.4	4.6	67.5	16.7
			3	2.7	0.11	20.6	5.8	-	67.6	5.0	*	20.3
			mean	3.4	0.12	20.6	5.8	0.02	63.5	4.8	67.5	18.5
			Std. dev.	NC	NC	NC	NC	NC	NC	NC	NC	NC
4	5	unfiltered	1	-	-	-	-	0.02	-	-	-	-
			2	4.0	0.11	21.1	*	0.03	73.8	4.2	78.9	20.8
			3	4.0	0.11	18.3	3.8	-	80.9	3.9	*	19.4
			mean	4.0	0.11	19.7	-	0.03	77.4	4.1	84.6	2.1
			Std. dev.	NC	NC	NC	-	NC	NC	NC	NC	NC
8	5		1	4.0	0.10	17.3	5.8	0.01	72.7	3.3	73.2	22.2
			2	4.0	0.09	17.8	4.4	-	58.4	3.4	73.2	23.1
			3	4.0	0.09	17.6	2.7	0.02	64.9	3.0	*	22.5
			mean	4.0	0.09	17.6	4.3	0.02	65.3	3.3	78.9	22.6
			Std. dev.	NC	0.01	0.3	1.6	-	7.2	0.2	9.9	0.5
6	5	unfiltered	1	4.0	0.10	19.7	*	0.02	57.4	4.5	61.8	24.9
			2	4.0	0.09	24.9	5.8	0.02	*	4.1	67.5	19.4
			3	2.7	0.09	22.3	5.8	0.04	62.3	3.9	*	21.7
			mean	3.6	0.09	22.3	7.1	0.03	68.5	4.2	64.7	22.0
			Std. dev.	0.8	0.01	2.6	2.2	0.01	15.2	0.3	NC	2.8
		Mean all data (unfiltered)		3.7	0.10	20.0	5.3	0.02	66.5	4.2	79.7	21.1
		±1 Std. deviation		0.7	0.01	2.4	1.2	0.01	8.0	0.6	12.0	2.3

* Omitted from mean - contamination suspected.
\- Indicates no data.
NC Indicates not computed.

Table 3.17.

Trace Metal Concentrations (Unfiltered) in the Main, East, Reindeer and Middle Channels, February 1 - 8, 1986 ($\mu mol \cdot m^{-3}$)

Channel	Location	Depth (m)	Cu	Cd	Pb	Zn	Cr	V	As	Ni	Hg (total)
Main	Centre	5	22.3	0.24	0.43*	42.4	5.2	92.0	3.51	47.9	0.020
			21.6	0.20	0.80	31.6	6.5	80.6	3.65	53.0	<0.015
		10	17.0	0.20	0.79	44.0	5.0	82.8	3.15	56.7	0.037
			21.0	0.23	0.73	41.8	6.4	76.0	3.07	54.3	0.032
			22.2	0.22	0.82	42.7	6.5	92.4	3.65	51.6	
	West	10	-	0.23	0.71	31.4	5.4	83.0	3.18	59.3	0.032
			21.6	0.20	0.82	42.0	6.5	80.4	3.54	53.0	0.027
	East	8	22.8	0.18	0.83	34.6	7.3	84.2	3.38	46.7	0.028
			20.3	0.20	0.79	31.0	6.8	86.0	3.12	54.3	0.029
			-	-	-	-	-	-	-	-	0.031
	Mean (all samples)		21.8 ±0.9	0.21 ±0.02	0.79 ±0.04	37.9 ±5.6	6.2 ±0.8	84.2 ±5.4	3.36 ±0.23	53.0 ±3.9	0.028 ±0.007

Table 3.17, cont'd.

Trace Metal Concentrations (Unfiltered) in the Main, East, Reindeer and Middle Channels, February 1 - 8, 1986 ($\mu mol \cdot m^{-3}$)

Channel	Location	Depth (m)	Cu	Cd	Pb	Zn	Cr	V	As	Ni	Hg (total)
East	Centre	3	29.0*	0.23	0.73	42.9	7.5	81.3	2.91	52.3	0.015
			21.6	0.20	0.80	-	5.0	-	3.30	54.3	0.016
		8	27.8*	0.18	0.73	37.2	5.0	86.0	5.31	50.4	0.034
			20.3	0.20	0.75	28.9	6.4	94.8	5.54	61.2	0.029
			19.1	0.20	0.80	40.0	3.7	95.6	3.28	51.8	-
	West	5	21.6	0.20	0.80	26.9	5.4	80.5	4.46	59.3	0.023
			20.3	0.19	0.75	40.0	-	114.6	-	-	-
				0.23	0.82	35.8	7.5	97.0	4.97	51.8	0.018
	East	5	20.3	0.20	0.83	31.4	5.0	80.5	5.30	53.0	0.024
			21.6	0.19	0.82	31.0	5.6	86.0	-	53.0	0.016
	Mean		20.7	0.20	0.78	34.9	5.7	90.7	4.38	54.2	0.022
			±1.0	±0.02	±0.04	±5.6	±1.3	±11.1	±1.07	±3.6	±0.006
Time Series	**Time**										
(East Channel, Centre 3m)	1		29.0*	0.23	0.73	42.9	7.5	81.3	2.91	52.3	0.015
			21.6	0.20	0.80	-	5.0	-	3.30	59.3	0.016
											0.021
	2		20.3	0.20	0.73	29.1	2.9	81.9	4.01	53.0	0.022
			21.6	0.19	0.75	32.6	6.4	92.0	3.30	51.8	0.022
	3		20.3	0.24	0.76	30.1	3.1	77.5	3.75	53.0	0.030
			19.1	0.20	0.82	27.5	6.4	84.0	3.40	52.3	0.027
			21.6	0.19	0.75	33.1	6.5	92.0	3.59	54.3	0.028
	Mean		20.8	0.21	0.75	32.6	5.4	84.8	3.47	53.7	0.023
			±1.0	±0.02	±0.03	±5.5	±1.8	±6.0	±0.36	±0.6	±0.005

* Contamination suspected: omitted from mean

Table 3.17, cont'd.

Trace Metal Concentrations (Unfiltered) in the Main, East, Reindeer and Middle Channels, February 1 - 8, 1986 ($\mu mol \cdot m^{-3}$)

Channel	Location	Depth (m)	Cu	Cd	Pb	Zn	Cr	V	As	Ni	Hg (total)
Reindeer	Centre	4	21.6	0.24	0.52	33.0	4.2	93.6	3.5	51.8	0.017
			22.8	0.20	0.70	41.0	5.0	80.4	-	-	0.033
		10	24.0	0.20	0.71	28.9	6.3	96.4	3.59	59.3	0.031
			21.6	0.22	0.79	26.9	6.5	-	3.15	59.3	
			22.8	0.18	0.73	33.0	5.5	88.6	3.23	60.4	0.033
	West	8	22.8	0.19	0.85	31.3	6.3	106.8	3.34	46.7	0.034
			21.6	0.23	0.80	-	5.4	92.5	3.30	53.0	0.027
	East	8	24.0	0.23	0.82	31.8	5.6	96.6	4.37	54.3	0.034
			20.3	0.20	0.73	33.0	5.8	93.4	3.70	53.0	0.034
	Mean		22.4	0.21	0.74	32.4	5.6	93.5	3.52	54.5	0.031
			±1.2	±0.02	±0.10	±4.1	±0.7	±7.5	±0.39	±4.7	±0.006
Middle	Centre	5	22.8	0.22	0.76	44.6	3.5	65.6	4.00	54.3	0.025
			22.8	0.18	0.85	31.0	6.5	95.6	4.21	50.4	0.019
		10	24.0	0.18	1.06	44.7	7.5	76.0	3.86	56.7	0.018
			24.0	0.20	0.74	-	6.5	93.4	4.46	51.8	0.018
	East	8	24.0	0.26	0.86	30.1	7.7	93.4	3.32	49.2	0.032
			21.6	0.22	0.85	33.8	7.5	94.8	4.37	53.0	0.030
	West	8	22.8	-	0.83	42.7	7.5	78.5	3.84	46.7	0.030
			20.3	0.23	0.79	-	6.3	84.0	3.65	49.2	0.039
	Mean		22.8	0.21	0.83	37.8	6.6	87.3	3.89	51.1	0.027
			±1.3	±0.03	±0.10	±6.3	±1.3	±12.1	±0.42	±3.1	±0.007

these differences are considered to be minor. However, for detailed winter flux estimates, these data suggest that measurements should be made in each of the outer three channels.

There were also no significant differences in Cu, Cr and Hg concentrations between sampling trips (1985, 1986) in the East Channel. There were however, quite large differences for some metals. It is felt that these differences are likely a result of calibration errors rather than real variations. Unfortunately there was no means of assessing accuracy in 1985 at actual river concentrations.

Cadmium concentrations in 1986 were about twice 1985 levels. At least part of the difference may be a calibration error. Analysis of SLRS-1 in 1986 gave results for Cd about 30% higher than the certified level. All river samples were higher than the reference material however. Conversely, 1985 concentrations may be low. Although there was agreement with NBS 1643 water concentrations, Cd concentrations were 100 times that in river samples.

Lead concentrations were almost 5 times lower in 1986 than in 1985. The 1986 levels are considered to be accurate based on the analysis of SLRS-1. In 1985, results were reproducible and as for Cd, excellent agreement was obtained with NBS reference material values. However, NBS levels were a factor of 10 - 50 greater than Pb levels in concentrated Mackenzie River samples. In addition, in 1986, the method of standard additions was used for calibration in concentrated samples because of matrix effects. In 1985 samples were calibrated via a standard curve using 2% HNO_3 in Milli-Q water. It is felt therefore that the 1985 concentrations may be in error and that the difference in concentrations in 1985 and 1986 is not a real variation.

Zinc concentrations were about 75% higher in 1986. As for Cd and Pb, it is not possible to assess the accuracy of 1985 results and hence whether the observed differences are real. In situ sampler results for dissolved levels are much lower than concentrations from discrete samples in 1986 but only slightly below concentrations found in filtered samples in 1985. Because of the apparently large proportion of Zn associated with particulates, the storage time and sample pretreatment may have a large influence on the final result. The present results therefore define a range of concentrations for these metals. Additional analyses will be required to more accurately define the variability of Zn, Cd and Pb.

Data from the East Channel for 1985 and 1986 are compared in Table 3.18 along with winter data from the Beaufort Sea Shelf in 1981-2 at Issungnak and other Arctic and Oceanic regions. Extrapolation of salinity versus metal concentration

Table 3.18.

Comparison of Trace Metal Concentrations in the East Channel, April 1985 and February 1986, and Concentrations for Beaufort Sea Shelf Water near Issungnak in March 1981 and other Oceanic Regions ($\mu mol \cdot m^{-3}$)

Date	Cu	Cd	Pb	Zn	Cr	V	Ni	As	Hg
April 1985	20.0 ±2.4	0.10 ±0.01	4.2 ±0.6	21.1 ±2.3	5.3 ±1.2	79.7 ±12.0	66.5 ±8.0	3.7 ±0.7	0.02 ±0.01
February 1986	20.7 ±1.0	0.20 ±0.02	0.78 ±0.04	34.9 ±5.6	5.7 ±1.3	90.7 ±11.1	54.2 ±4.6	4.38 ±1.07	0.02 ±0.01
(means of all data ± 1 standard deviation)									
Issungnak (Erickson et al., 1983)	6.6 ±0.4	0.61 ±0.08	-	11.8 ±2.4	2.6[a] ±0.4	-	-	-	0.01-0.20[b]
Upper 200 m Central Arctic Ocean (Moore, 1981)	2-5.4[b]	0.2-0.6[b]	-	2.3-6[b]	-	-	-	-	-
Compiled Oceanic Data (Forstner and Wittmann, 1979)	0.6-1.6[b]	0.09-0.6[b]	0.005-0.07[b]	0.15-9.2[b]	1.5-2.9[a,b]	37	3.4-12[b]	28[a]	0.01

a. Total Metal
b. Range

relationships of Mackenzie River diluted shelf water near Issungnak in the winter of 1982 (Erickson et al., 1983) gave river (0 salinity) concentrations of 2-3 $\mu mol \cdot m^{-3}$ for Zn and 25 $\mu mol \cdot m^{-3}$ for Cu. The results from this study confirm the expected trend for Cu (levels of about 22 $\mu mol \cdot m^{-3}$ for discrete samples; up 25 $\mu mol \cdot m^{-3}$ for in situ sampler samples).

Zn concentrations for unfiltered river samples are an order of magnitude greater than predicted and (calculated "dissolved" levels) 5 - 6 times higher. In situ sampler levels however were in the range of 4-7 $\mu mol \cdot m^{-3}$ only slightly higher than predicted. Since a large portion of Zn appears to be particulate or absorbed onto particulates, interpretation of trends is more complicated because of varying particulate loads, and means of sample pretreatment. The Mackenzie River nevertheless appears to be a source of total (dissolved and acid exchangeable) Zn to the Shelf. Evidently, a large portion of the river-borne particulate associated Zn is removed on mixing with saline shelf waters.

The expected concentrations of other metals in shelf water based on recent world ocean levels indicate the river is likely a winter source of Ni, Pb, Cr and V.

Arsenic and Cd concentrations however, are considerably lower in river water than in the oceans and Beaufort Sea Shelf. River water therefore dilutes levels of these metals in shelf waters. Cd concentrations of less than 0.2 $\mu mol \cdot m^{-3}$ appear to be a characteristic of many large rivers. Moore (1981) predicted a level of 0.09 $\mu mol \cdot m^{-3}$ for rivers entering the Arctic Ocean. Concentrations of Cd in the St. Lawrence River were 0.13 $\mu mol \cdot m^{-3}$ in reference water (SLRS-1) while Boyle et al. (1982) found a level of less than 0.1 $\mu mol \cdot m^{-3}$ for the Amazon River. Arsenic concentrations appear to be more variable. Forstner and Wittmann (1979) cited a mean of 27 $\mu mol \cdot m^{-3}$ for As in river water but St. Lawrence River water collected for the NRC reference material had a concentration of 7.3 $\mu mol \cdot m^{-3}$, slightly higher than concentrations found in the Mackenzie River.

Mercury concentrations are close to the detection limit and variability is high. River concentrations are not significantly different from the reported concentrations for oceanic water and results from Issungnak.

Since solute concentrations tend to vary inversely with flow, the concentrations of various trace metals observed during winter flows probably represent near maximum levels.

3.6.1 Dissolved vs Particulate Metals

Measurement of total and dissolved metal concentrations directly is difficult because of the low concentrations. In this study, particulate metal concentrations were determined on the basis of the analysis of a limited number of samples on filters or from centrifugation. The traditional means of determining dissolved concentration is to filter samples through 0.4 µm filters with any metal passing through being defined as "dissolved". Any clay material (< 0.2 µm) will therefore be included. Filtration of samples does entail extra handling and the possibility of contamination even when filtration equipment has been cleaned. In 1985, filtration was found to have contaminated samples for Cu. For most other metals, with the exception of Zn, there was no significant difference between filtered and unfiltered values. Therefore in 1986, samples were not filtered.

Particulate metal concentrations on a volume basis and metal levels in unfiltered water samples are summarized for each metal and channel in Tables 3.19 to 3.27. It is difficult to estimate the proportion of particulate metal that is analyzed in a direct injection analysis of water by graphite furnace atomic absorption. Unfiltered samples will give a measure of the dissolved plus readily acid leachable particulate metal. Particulates will be injected into the furnace with the water however and a further proportion of the particulate metal should be measured. However, with the exception of Zn, there was no significant (alpha = 0.05) difference between filtered and unfiltered results even where particulate metal concentrations were high. It is therefore assumed that the water analysis is primarily that of dissolved metal and that the particulate and water concentrations need to be summed to give a total metal value. On this basis, a percentage dissolved metal was estimated for each metal. For most metals >80% of the total is dissolved. However, about 65 - 70% of Cr appears to be particulate. Lead concentrations appear to be about 1:1 dissolved to particulate while between 40 - 60% of total zinc is dissolved.

3.6.2 In Situ Sampler

The columns used in April 1985 did not extract metals as expected. Analysis of the eluates from the columns gave results for all metals that were less than 10% of discrete sample values. Subsequent testing of the columns in the lab confirmed poor recovery. It is unclear why the resin material was not effective. Columns may have frozen and fractured the resin. High flow rates (200 $mL \cdot min^{-1}$) were also used.

Table 3.19.

Dissolved and Particulate Copper Concentrations
concentrations in $\mu mol \cdot m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	3.3	20.0	c	23.3	86
East	1986	4.5	20.7	19.2 (n=3)	23.7	81
Main	1986	7.9	22.8	19.0 (n=4)	26.9	71
Reindeer	1986	5.0	22.4	19.6 (n=3)	24.6	80
Middle	1986	4.6	22.8	20.1 (n=3)	24.7	81

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered" "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.
c - All samples filtered in 1985 were contaminated with Cu.

Table 3.20.

Dissolved and Particulate Nickel Concentrations
concentrations in $\mu mol \cdot m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	2.6	66.5	81.6	69.1	96
East	1986	5.3	54.2	55.0 (n=3)	59.5	91
Main	1985	4.3	53.0	51.2 (n=4)	55.5	92
Reindeer	1985	3.1	54.5	53.0 (n=3)	56.1	94
Middle	1986	3.9	51.1	52.2 (n=3)	55.0	93

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered" "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.

Table 3.21.

Dissolved and Particulate Lead Concentrations
concentrations in $\mu mol.m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	0.66	4.2	4.2	4.86	86
East	1986	0.62	0.78	c	1.40	56
Main	1986	1.06	0.79	c	1.85	43
Reindeer	1986	0.85	0.74	c	1.59	47
Middle	1986	0.99	0.83	c	1.82	46

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.
c - All higher or equal to unfiltered results.

Table 3.22.

Dissolved and Particulate Chromium Concentrations
concentrations in $\mu mol.m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	10.4	5.3	5.2	15.6	33
East	1986	12.6	5.7	b	18.3	31
Main	1986	14.3	6.2	b	20.5	30
Reindeer	1986	10.8	5.6	b	16.4	34
Middle	1986	10.4	6.6	b	17.0	39

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.

Table 3.23.

Dissolved and Particulate Mercury Concentrations
concentrations in $\mu mol \cdot m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	0.005	0.02	0.03	0.025	80
East	1986	0.002	0.002	N/A	0.024	92
Main	1986	0.003	0.028	N/A	0.031	90
Reindeer	1986	0.002	0.031	N/A	0.033	94
Middle	1986	0.002	0.027	N/A	0.029	93

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.
N/A - Not analyzed.

Table 3.24.

Dissolved and Particulate Zinc Concentrations
concentrations in $\mu mol \cdot m^{-3}$

Channel	Year	Particulate	Water Water Unfiltered	Dissolved* Dissolved* from Filtered Samples	Total[a] Total[a]	Percent Percent Dissolved[b]
East	1985	13.8	21.1	9.4 (n=6)	23.2	41
East	1986	14.4	34.9	20.9 (n=2)	35.3	59
Main	1986	18.1	37.9	18.2 (n=3)	36.3	50
Reindeer	1986	16.8	32.4	18.4 (n=3)	35.2	52
Middle	1986	9.4	37.8	c	c	c

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.
c - All filtered samples greater than unfiltered, contamination assumed, total not computed.

Table 3.25.

Dissolved and Particulate Cadmium Concentrations
concentrations in $\mu mol.m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	0.025	0.10	0.14	0.13a	80
East	1986	0.032	0.20	0.21 (n=3)	0.23	86
Main	1986	0.033	0.21	0.21 (n=4)	0.24	86
Reindeer	1986	0.030	0.21	0.20 (n=3)	0.24	87
Middle	1986	0.025	0.21	0.21 (n=3)	0.24	89

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered"
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.

Table 3.26.

Dissolved and Particulate Arsenic Concentrations
concentrations in $\mu mol.m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East	1985	N/A	3.7	4.0	NC	NC
East	1986	0.438	4.38	3.3 (n=3)	3.74	88
Main	1986	0.659	3.36	3.4 (n=3)	4.02	74
Reindeer	1986	0.455	3.52	3.5 (n=3)	3.98	89
Middle	1986	0.646	3.89	3.4 (n=3)	4.05	74

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered" "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.
N/A - Not analyzed.
NC - Not computable.

Table 3.27.

Dissolved and Particulate Vanadium Concentrations
concentrations in $\mu mol.m^{-3}$

Channel	Year	Particulate	Water Unfiltered	Dissolved* from Filtered Samples	Total[a]	Percent Dissolved[b]
East		12.6	79.9	82.9	92.3	86
East		15.4	90.7	92.0 (n=3)	106.1	85
Main		21.1	84.2	90.4 (n=4)	105.3	80
Reindeer		15.7	93.5	87.3 (n=3)	103.0	85
Middle		13.4	87.3	90.4 (n=3)	100.7	87

* - Mean of all filtered samples.
a - "Total" calculated as "Particulate" + "Dissolved from Filtered Samples", except where "Dissolved from Filtered Samples" is unknown or is greater than "Water Unfiltered". "Total" was calculated as "Particulate" + "Water Unfiltered".
b - "Percent Dissolved" calculated as (1 - "Particulate"/Total) x 100.

Both factors may have contributed to low recovery. Although the exact cause is uncertain, alteration of the resin material as a result of freezing seems most likely.

In 1986, care was taken to ensure columns were not frozen and slower (100 $mL \cdot min^{-1}$) flow rates were used. Results from the samples collected in 1986 are presented in Table 3.28, where they are compared to mean results for dissolved metals from discrete samples for each channel. As expected the extraction efficiency for metals such as Cr and V with bonded 8-hydroxyquinoline is low. Although arsenic was not tested, extraction efficiencies with 8-hydroxyquinoline in natural waters are also low. Laboratory development work with the resin had indicated Hg was extracted quantitatively but could not be eluted from the column.

Cadmium results were variable. The sample from the Main Channel gave an over recovery (75% high) while concentrations for the columns from other channels were low (43-62% of discrete samples). Quantitative recovery of Cd had been expected on the basis of laboratory performance. The apparent low recoveries from three channels may be a result of in situ extraction as opposed to the long term storage at pH <2 for discrete samples. The low in situ sampler results agree with East Channel 1985 results and concentrations in other major river systems.

Cu concentrations from the in situ samplers were in close agreement in all channels and with the discrete sample results. For Ni, recoveries from the columns agreed closely with the discrete sample results except for the Middle Channel sample which was almost twice the concentration of other in situ sampler derived and discrete sample concentrations. For Pb, all in situ sampler concentrations were in close agreement with each other and the discrete sample concentrations (less than 10% deviation).

In situ sampler derived zinc concentrations were in close agreement with each other but lower than calculated dissolved concentrations based on filtered water and particulate metal concentrations by a factor of three. The observed Zn concentrations from the columns are in closer agreement with the results from 1985. As noted previously, Zn concentrations in 1986 are systematically higher than in 1985 by about 75%. The apparent low in situ sampler recoveries in 1986 may be real or may be in part due to 1986 concentrations for discrete samples being erroneously high. Apparent low recoveries for Zn may also reflect sample treatment. Discrete samples were stored acidified (pH < 2) for several months prior to analyses. Since a large portion of the Zn is evidently asociated with particulates, some Zn, even in filtered samples, will be from particulates. With the in situ sampler however, water is extracted at the ambient pH level and there is no prior storage. Given the proven

Table 3.28.

Summary of In Situ Sampler Data for Trace Metals Using XE305/8-hydroxyquinoline Columns

Channel	Metal ($\mu mol \cdot m^{-3}$)									
	Cu		Cd		Pb		Zn		Ni	
	S	D	S	D	S	D	S	D	S	D
East (1985)	All results for in situ sample <10% of discrete sample values.									
East (1986)	22.4	20.7 ± 1	0.35	0.20 ± 0.02	0.88	0.78 ± 0.04	6.8	20.9	49.0	54.2 ± 3.6
East (Feb. 8 - March 11, 1986)	22.8	-	0.25	-	1.09	-	4.4	-	58.0	-
Main	23.6	21.8 ± 0.9	0.13	0.21 ± 0.02	0.85	0.79 ± 0.04	4.7	18.2	61.2	53.0 ± 3.9
Reindeer	23.5	22.4 ± 1.2	0.09	0.21 ± 0.02	1.10	0.74 ± 0.10	5.4	18.4	54.0	54.5 ± 4.4
Middle	23.8	22.8 ± 1.3	0.12	0.21 ± 0.02	0.78	0.83 ± 0.10	5.0	-	113.0	51.1 ± 3.1

S = in situ sampler

D = dissolved metal from discrete samples

Note: Cr in situ sampler concentrations less than 0.5 $\mu mol \cdot m^{-3}$.
V in situ sampler concentrations were 20% or less of discrete sample results.

ability of the resin material to quantitatively extract Zn, it seems likely that the in situ sampler results more closely represent actual "dissolved" Zn concentrations.

The XE-305/8-hydroxyquinoline columns therefore appear to give quantitative recoveries for Cu, Pb, Ni and possibly Zn although contamination seems to have occurred in one column eluate for Ni.

3.7 Hydrocarbons

A series of procedural blanks were carried through each method and the blank mean and standard deviation determined after analysis by the appropriate instrumental method. The absolute detection and quantification limits in nanograms for each compound were defined as three or nine standard deviations of the mean procedural blank respectively (Keith et al., 1983).

An analysis of variance was done for several hydrocarbon parameters using only the particulate data as the dissolved hydrocarbons were generally below the quantification limit for all samples. Differences for total alkane, total PAH, nC29 alkane, C3-naphthalene, odd-even predominance, particulate organic carbon and suspended particulate material were tested for significance between channels, by sample depth, by sampling trip and by position across channel. No significant differences (alpha = 0.05) could be found for any of these parameters except suspended particulate material for which there was a significant difference between channels. Consequently the hydrocarbon data for all samples are treated as a set without differentiation between channels, depths, locations across channels or sample trips.

3.7.1 Dissolved Hydrocarbons

A suite of twenty-six 4 L NBS bottle samples and three in situ sampler column samples collected in April 1985 were filtered, extracted and analyzed by UV-fluorescence. All samples were found to be below the detection limit of 2 $\mu g \cdot L^{-1}$ Norman Wells crude equivalents. Combined extracts from eight 4 L bottle samples

(32 L) were concentrated but the PAHs were still below the UV-fluorescence detection limit. However, GC/FID and GC/MS analyses of these combined water extracts indicated low concentrations of petroleum hydrocarbons. Subsequently all analyses were performed by GC/FID and GC/MS and larger sample volumes were collected or processed.

Trace levels of dissolved hydrocarbons were discernable in 1986 bottle sample extracts but concentrations found for most of the monitored hydrocarbons (nonpolar and aromatic) in the filtered bottle samples were below the detection limit. Background hydrocarbons in nonpolar and aromatic fractions became dominant at the high sensitivity and extreme preconcentration conditions used, masking the sample components. The mean concentrations of total alkanes (nC12 to nC36) and total PAHs in the dissolved phase were less than 74 $ng \cdot L^{-1}$ and 30 $ng \cdot L^{-1}$ respectively (Table 3.29). A possible exception was the presence of quantifiable levels of alkyl naphthalenes, notably C-3 naphthalene which was found at low but consistent levels (5.8 $ng \cdot L^{-1}$ mean for 20 x 18 L bottle samples, standard deviation = 2.9 $ng \cdot L^{-1}$).

Higher molecular weight alkane concentrations are comparable to the quantification limits. However, the mean odd-even predominance for filtered bottle samples is 1.097 and is similar to the blank which suggest these alkanes are largely analytical artifacts. Typical bottle sample and blank GC traces for dissolved nonpolar hydrocarbons are given in Figure 3.5.

Detection limits for 18 L samples were in the range of 2 to 10 $ng \cdot L^{-1}$ for individual alkanes and 0.1 to 1.0 ng for individual aromatics except for naphthalene which had an elevated blank.

Dissolved hydrocarbons eluted from the in situ sampler columns were at or below detection limits for the PAHs and nonpolar hydrocarbons (Tables 3.29), despite generally lower detection limits for the in situ sampler XAD-2 columns than for the bottle samples. Concentrations of dissolved total alkanes and PAH determined for bottle and in situ samples are less than the detection limits but are given for comparison (Table 3.29) between sampling methods and provide a maximum value for the calculation of a hydrocarbon flux. Typical column and blank column GC traces are shown in Figures 3.6 and 3.7. Typical aromatic blanks are given in Table 3.30. The alkyl naphthalenes are below detection limits but show a similar relative abundance as for the bottle extracts although at a lower level (0.87 $ng \cdot L^{-1}$ mean C3-naphthalene) than in the bottle samples (5.8 $ng \cdot L^{-1}$).

Table 3.29.

Summary of Hydrocarbon Data

a) Mean total alkanes and total PAH ($ng \cdot L^{-1}$)

Sampling Method	Dissolved		Particulate	
	Total Alkane	Total PAH	Total Alkane	Total PAH
Bottle sample	< 74 (n=20)	< 30 (n=20)	30, s 12 (n=20)	< 34, (n=20)
In situ sampler	< 23 (n=7)	< 72 (n=6)	18, s 5 (n=6)	7.9, s 1.9 (n=7)
Continuous-flow centrifuge	-	-	14, s 4 (n=4)	3.0, s 0.8 (n=4)

b) Mean values for nC29 and C3-napthalenes ($ng \cdot L^{-1}$)

Sampling Method	Dissolved		Particulate	
	nC29	C3 naphthalene	nC29	C3 naphthalene
Bottle sample	9.1 (n=20)	5.8 (n=20)	4.1, s 1.4 (n=20)	< 9.3 (n=20)
In situ sampler	< 2.6 (n=7)	< 3.2 (n=6)	3.0, s 0.6 (n=6)	1.4, s 0.2 (n=7)
Continuous-flow centrifuge	-	-	2.7, s 1.5 (n=4)	< 0.5 (n=4)

c) Odd-even predominance for alkanes at nC29.

Sampling Method	Dissolved	Particulate
Bottle sample	N.A.	1.7
In situ sampler	N.A.	2.5
Continuous-flow centrifuge	-	2.6

d) Phenanthrene:anthracene ratios.

Sampling Method	Dissolved	Particulate
Bottle sample	N.A.	N.A.
In-situ sampler	N.A.	6.7
Continuous-flow centrifuge	-	N.A.

N.A. not available; concentrations below detection limit

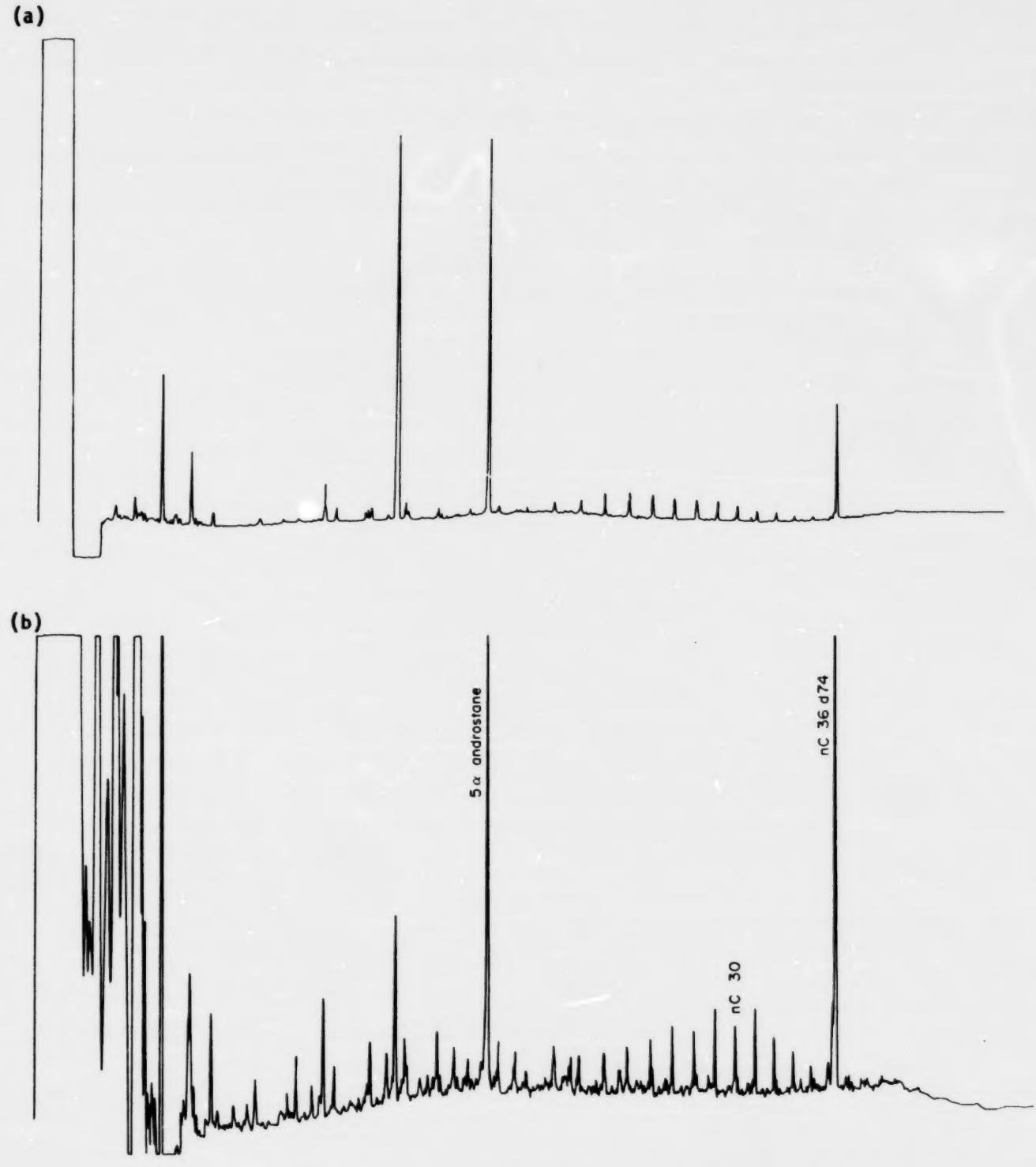


Figure 3.5. GC/FID chromatograms of nonpolar hydrocarbons from (a) procedural blank, and (b) typical 18 L water sample extract (NW-2-15W, East Channel, centre hole, 3 m).

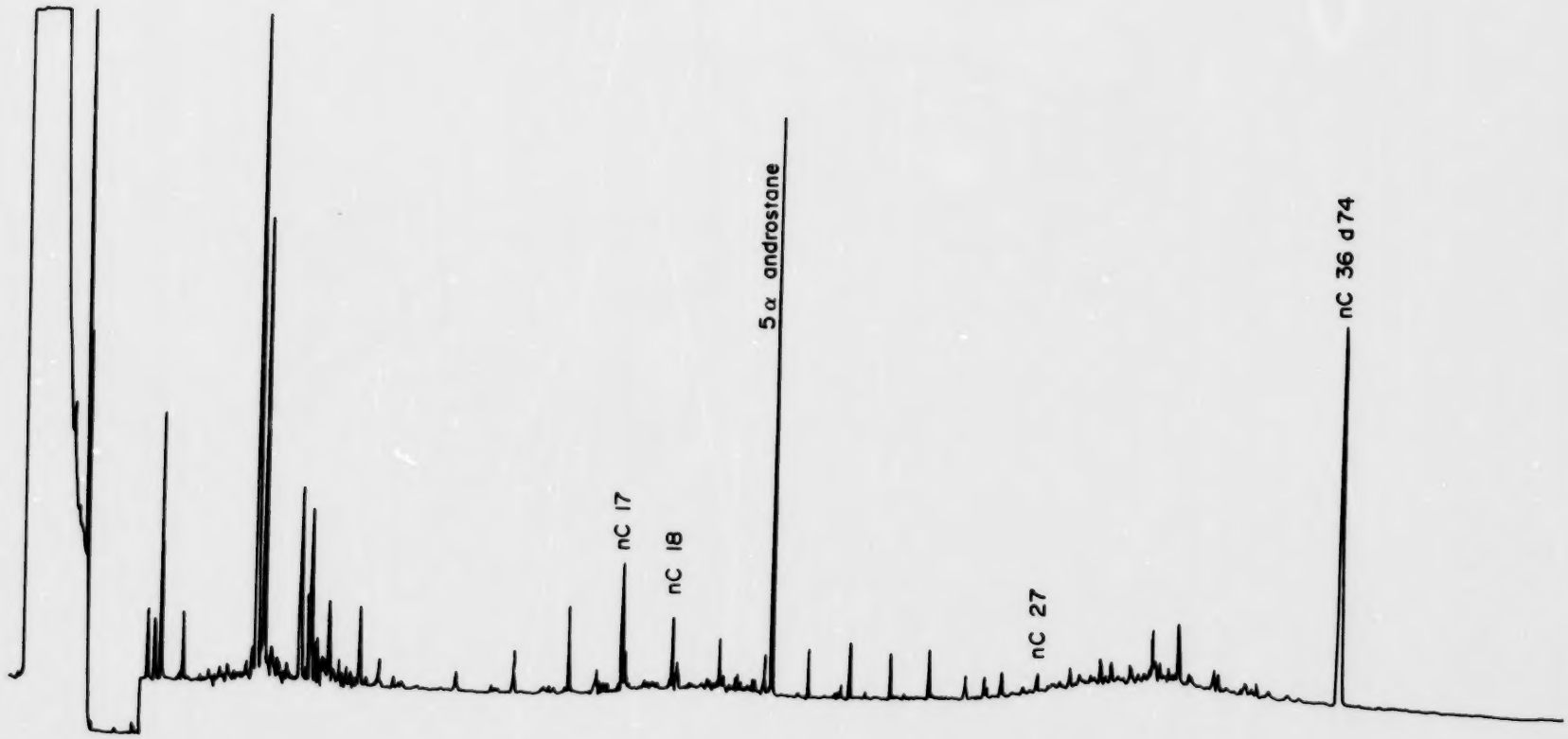


Figure 3.6. GC/FID chromatogram of nonpolar hydrocarbons from an XAD-2 column blank.

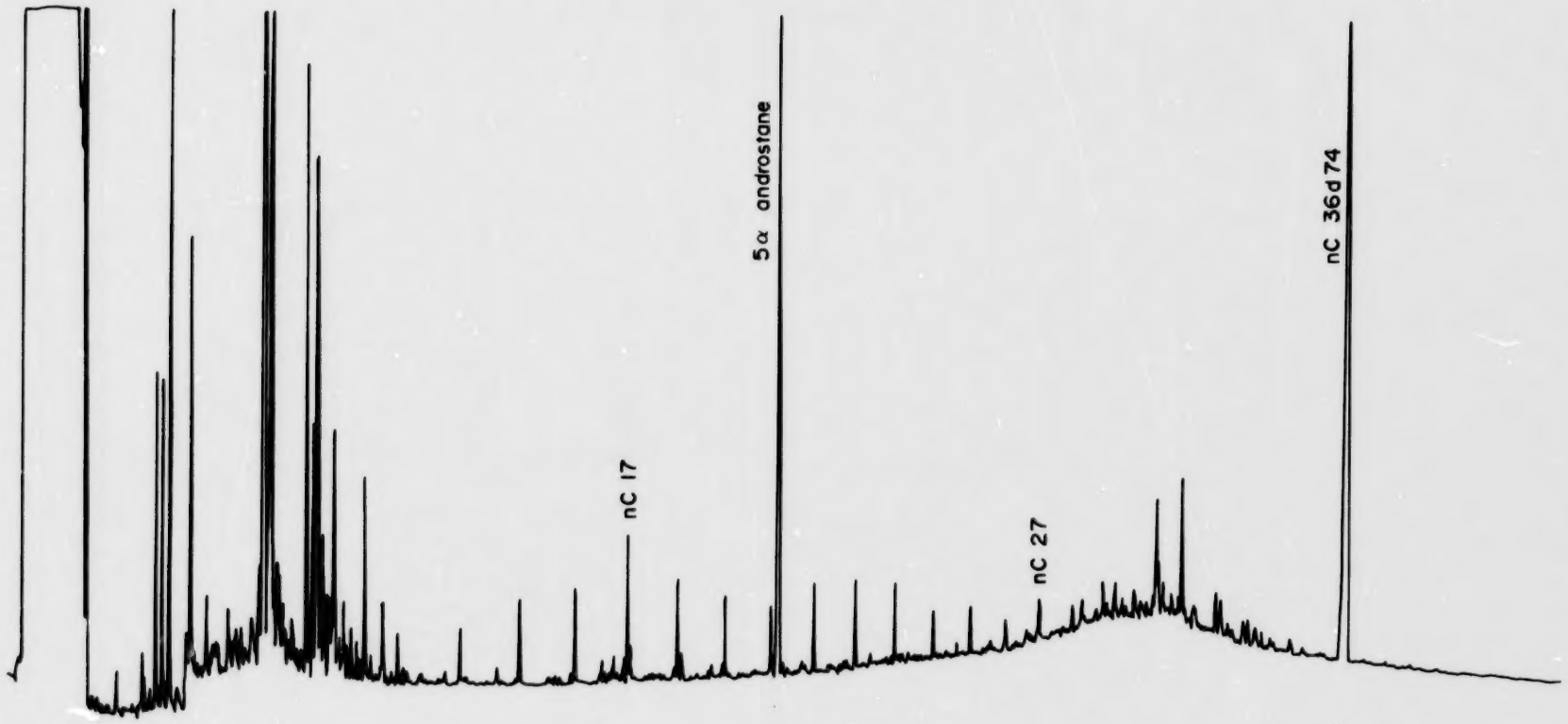


Figure 3.7. GC/FID chromatogram of nonpolar hydrocarbons from a typical XAD-2 in situ sampler column extract (ISS-3-1C, East Channel, centre hole, 5 m).

Table 3.30.

Column PAH Blanks
(Limits for 50 L)

Compound	Detection Limit	Quantitation Limit
Naphthalene	55.4	137.5
Fluorene	0.5	1.4
Phenanthrene	1	2.7
Anthracene	0.2	0.5
Fluoranthene	1	2.8
Pyrene	0.1	0.2
Benz(a)anthracene	0.3	0.7
Chrysene	0.4	1.1
Benzofluoranthenes	0.3	0.6
Benzo(e)pyrene	0.4	1
Benzo(a)pyrene	0.6	1.5
Perylene	0.6	1.5

Note: Detection limit calculated as mean + 3 x standard deviation.
Quantitation limit calculated as mean + 9 x standard deviation.

3.7.2 Particulate Hydrocarbons

A suite of alkanes were present at quantifiable levels in particulate samples (bottle sample, in situ samples and Sedisamp continuous centrifuge). Bottle sample filters from twenty 18 L samples were at low levels approaching that of the blanks, and the lower alkanes (nC10 to nC22) were at or below the detection limits. The higher molecular weight alkanes nC24 to nC36 were quantifiable and qualitatively different from the blanks. A distinct odd carbon predominance is apparent in all these particulate samples characteristic of terrestrial plant wax derived hydrocarbons (Table 3.29). Only the higher alkanes nC25 to nC36 are considered in the calculation of total alkanes, and for the bottle samples, the mean total alkanes for 20 samples was 29.6 $ng \cdot L^{-1}$, (standard deviation 12.1 $ng \cdot L^{-1}$). Other petroleum hydrocarbon indicator parameters such as pristane:phytane ratios, nC18:phytane ratios and alkane:isoprenoid ratios (Boehm, 1981) were not reliable as these parameters utilize results which were generally below the detection limit.

In situ sampler filters showed similar features (Figure 3.8) and, due to improved detection limits with larger sample volumes, showed a wider range of quantifiable compounds. The mean alkane levels were consistently lower than with bottle filters by 20 to 40% for the higher alkanes. The reason for this is unclear but may be a systematic error of the sampler or filter system used.

The nonpolar hydrocarbons found in the continuous-flow centrifuge sediments were similar qualitatively and quantitatively with the in situ sampler particulate alkanes, with a generally improved detection limit, due to larger sample volumes. The composition of nonpolar hydrocarbons is typical of terrestrial plant wax derived hydrocarbons with a distinct odd carbon preference (mean OEP at nC29 = 2.58; see Table 3.31) and is comparable to surficial sediment samples of the nearshore Beaufort Sea (typical OEP 1.6-1.7; see Table 3.31). When converted to a weight basis (ng hydrocarbon per g sediment), the suspended sediment appears to have comparable values to Beaufort Sea sediments (Table 3.31, Comparison of Sedisamp nonpolar hydrocarbons to Beaufort Sea Sediment results is shown in Figure 3.9.)

Compared to the bottle samples, the Sedisamp nonpolar hydrocarbons were significantly lower (48% of the bottle filter levels) and this may be a result of lower recoveries for the Sedisamp as discussed in Section 3.2.1.1 This would account for the finding that the Sedisamp gave consistently lower nonpolar and aromatic values than the other two sampling methods (Table 3.28).

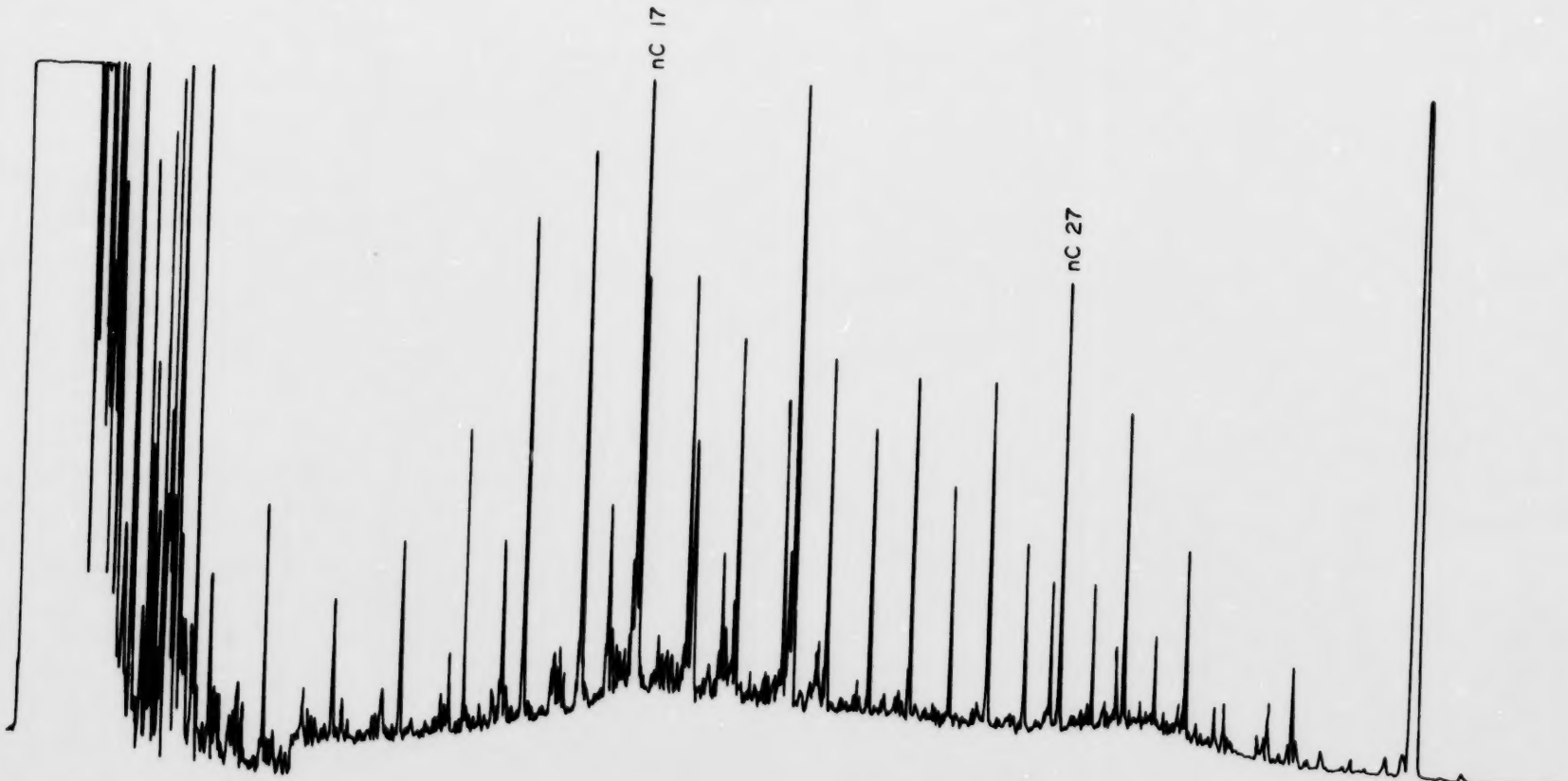


Figure 3.8. GC/FID chromatogram of nonpolar hydrocarbons from an in situ sampler filter extract (ISS-3-1F, East Channel, centre hole, 5 m).

Table 3.31

Comparison of Hydrocarbon Concentrations on Suspended Sediment to Beaufort Sea Surface Sediment ($ng \cdot g^{-1}$, dry wt.)

	nC17	nC29	Total Alkanes	OEP	C3-naphthalene	Phenanthrene	Total PAH
Mackenzie Particulate							
Middle	590	370	2400	2.15	140	33	560
Reindeer	550	450	2900	2.49	180	55	710
Main	790	730	4100	2.61	200	53	600
East	420	370	2200	3.08	210	35	420
Beaufort Sea							
Minuk[a]	740	365	3000	1.60	110	34	2000
Kaubvik[b]	590	235	1800	1.70	50	110	710

a) 2 km due east of Minuk artificial island, 69°42'N, 136°24'.

b) 2 km due east of Kauvik artificial island, 69°52'N, 135°44'.

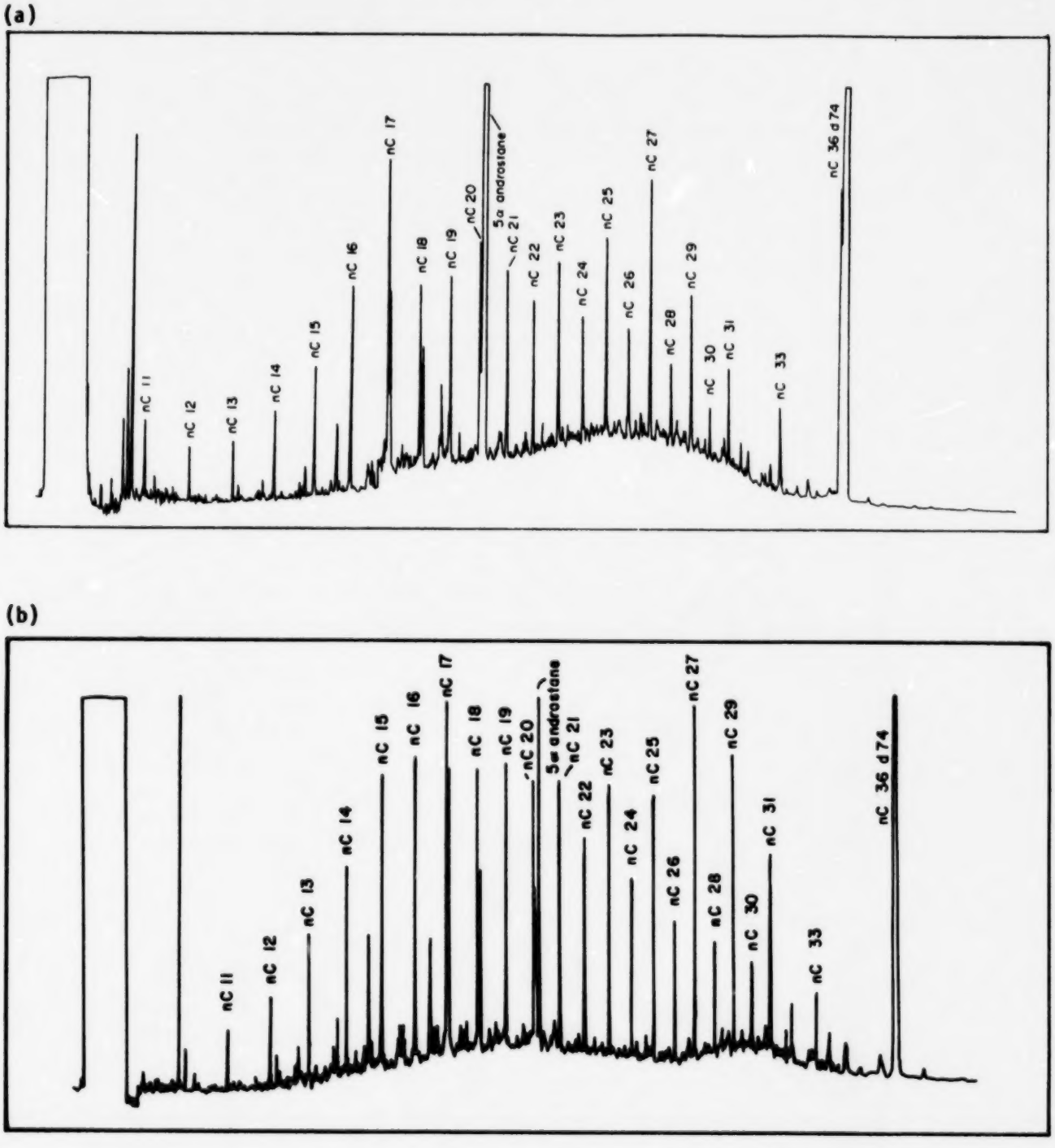


Figure 3.9. GC/FID chromatograms of nonpolar hydrocarbon from:
(a) sediment collected by the continuous-flow centrifuge;
(b) Beaufort Sea surficial sediment (Minuk Island, 14 m, sample 1-18).

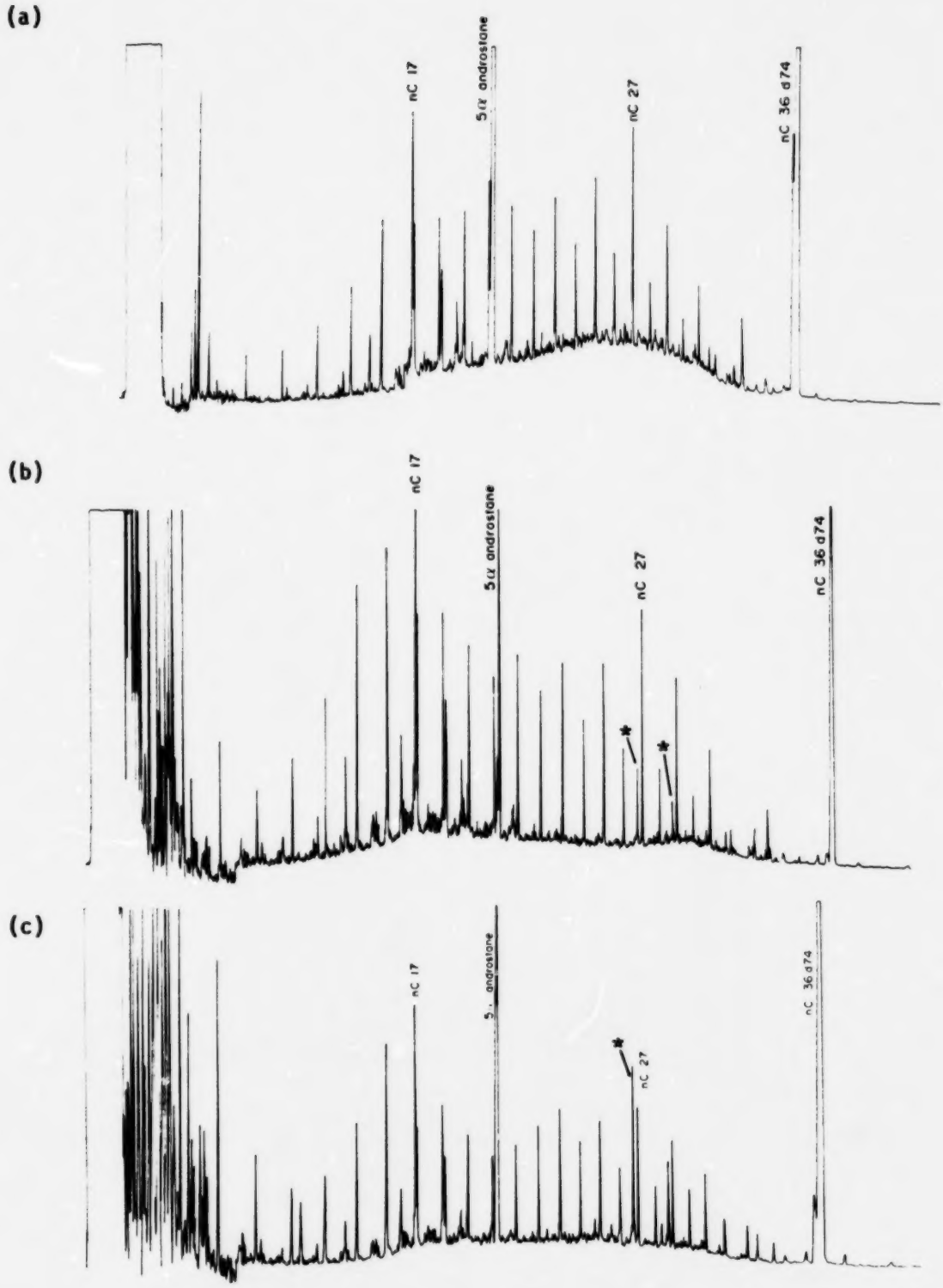


Figure 3.10. GC/FID chromatogram of nonpolar hydrocarbons on sediment collected by (a) continuous-flow centrifuge; (b) in situ sample filtration onto a glass fibre filter; and (c) bottle sample filtered onto glass fibre filter. * denotes peaks absent in (a).

Table 3.32.

Comparison Total Nonpolar Hydrocarbon Concentrations by Filtration and Continuous-Flow Centrifuge

Channel	Total Nonpolar Hydrocarbons (µg.m-3)		
	Centrifuge	Filtration	%[a]
Middle	11.2	27.7	40.4
Reindeer	14.4	26.6	54.1
Main	19.3	35.6	54.2
East	11.4	29.1	39.2

a) centrifuge as % of filtered value.
( ) indicates number of replicates analyzed.

Table 3.32.

Concentration of Chlorinated Hydrocarbons ($pg.L^{-1}$)

Compound	Dissolved		Particulate	
	ISS[a] April 1985	ISS[b] February 1986	ISS[b] February 1966	Sedisamp[c] February 1986
alpha-BHC	4900	3000	< 1	10
gamma-BHC	500	400	< 1	< 1
HCB	< 10	< 9	6	10
aldrin	< 10	< 5	< 4	< 0.6
dieldrin	< 5	< 5	< 4	< 0.6
heptachlor	< 5	< 5	< 4	< 0.6
heptachlorepoxide	< 20	50	< 10	< 1
o,p'-DDT	< 30	< 20	< 20	< 3
p,p'-DDT	< 30	< 20	< 20	< 3
o,p'-DDE	< 20	< 10	< 10	< 2
p,p'-DDE	< 20	< 10	< 10	< 2
o,p'-DDD	< 20	< 20	< 20	< 2
p,p'-DDD	< 20	< 20	< 20	< 2
trans-chlordane	< 10	< 10	< 4	< 0.6
cis-chlordane	< 20	90	< 4	< 0.6
endrin	< 5	< 20	< 10	< 3
alpha endosulphan	< 10	< 10	< 10	< 3
PCB (Arochlor 1254)	< 100	< 90	< 90	< 6

a) East Channel, hole 5, 54.34 L pumped.
b) Reindeer Channel, centre hole, 69.01 L pumped.
c) East Channel, effectively 495 L pumped.

Aromatic hydrocarbons were present at a low level on all bottle filters but were below quantification limits. In situ sampler filters gave a qualitatively similar composition, but at quantifiable levels.

As with the nonpolar hydrocarbons, the aromatic composition was very similar to nearshore Beaufort Sea surficial sediments and, on a weight basis, were quantitatively similar (Table 3.31).

3.7.2.1 Comparison of Hydrocarbons in Particulates Obtained by Filtration and Centrifugation.

Qualitatively, the particulate nonpolar hydrocarbons from bottle samples, the in situ sampler or the continuous centrifuge were very similar, particularly for the higher boiling compounds (nC24 and higher). Minor compositional differences may be accounted for by differing blank contributions which decrease with increasing water sample volume. A conspicuous difference is the presence of minor non-alkane compounds appearing as peaks at around nC27 and nC29 (Kovat's indices 2672.7 and 2875.0 respectively) in the bottle and in situ sampler filters but not in the continuous-flow centrifuge samples (Figure 3.10). These peaks may be compounds associated with less dense biological material not retained by the centrifuge. Fractionation by density for continuous-flow centrifuge sampling has been previously reported (Duinker et al., 1979; Ongley and Blachford, 1982).

A comparison of the total nonpolar hydrocarbon concentrations found by these methods (see Table 3.32) also indicates a low particulate recovery by the centrifuge.

3.8 Chlorinated Hydrocarbons

Chlorinated hydrocarbons were determined in two in situ sampler columns, on an in situ sampler filter and on continuous-flow centrifuge sediment. Results are given in Table 3.33. In the dissolved phase, two hexachlorocyclohexane isomers alpha-BHC and gamma-BHC were found in comparable levels and composition in spring 1985 and winter 1986. Trace levels of cis-chlorodane and heptachlor epoxide were also found in the winter 1986 sample.

The only target chlorinated compound found in the particulate phase was hexachlorobenzene (HCB) which was present at low levels in both particulate samples.

Both dissolved and particulate samples showed very low levels with very few chlorinated compounds and there is no evidence of significant levels of any chlorinated compound outside of the 17 target compounds. There is a striking difference between the distribution of BHC and HCB between phases, with BHC present almost entirely in the dissolved and HCB only in the particulate.

4. FLUX OF HYDROCARBONS, TRACE METALS AND NUTRIENTS

It is possible with the data collected in this study to calculate a flux of dissolved and particulate trace metals, hydrocarbons and dissolved nutrients through the outer channels of the Delta for the low flow winter period. Table 4.1 summarizes these estimates using discharges calculated by IWD for each channel and mean concentrations of each variable in 1986 and compares these estimates to annual fluxes estimated by Thomas et al. (1983). If the data are considered representative of the period December 1 to May 9 (160 days or 0.44 years) it can be seen that the winter flux of all variables is a very small percentage of the estimated annual flux. The winter SPM flux is a factor of 106 below the annual estimate so that the winter particulate chemical flux will be an insignificant part of the annual total. The dissolved winter flux is probably significant, however. Comparisons with annual totals are difficult as there is no comparable data for trace metals and hydrocarbons for the rest of the year. Trace metal data previously available for instance for Cd and other elements appear to be at least one order of magnitude too high. No other hydrocarbon data for either the winter or summer is available for comparison. Dissolved levels of many metals as well as hydrocarbons may be higher in winter in concert with higher levels of major cations. Thus, although flows are much reduced, the net flux of dissolved metals and hydrocarbons will not be reduced in proportion to the reduced discharge.

Table 4.1.

Winter Flux of Nutrients, Trace Metals and Hydrocarbons from the Mackenzie River to the Beaufort Sea through the East, Middle and Reindeer Channels, 1986.

Chemical Variable	Dissolved		Particulate		Total Flux (daily) (mol)	Winter Flux Total (160 days) (mol)	Total Estimated[c] Annual Flux (mol)	Comments
	Mean Concentration[a]	Flux[b] (daily) (mol)	Mean Concentration[a]	Flux[b] (daily) (mol)				
As	3.4	817	0.49	119	936	1.5 x105	-	
Cd	0.21	51	0.029	7.0	58	4.48 x103	4.9 - 13.1 x106	
Cr	6.0	1.45 x103	11.4	2.74 x103	4.19 x103	6.7 x105	6.4 - 6.8 x107	
Cu	19.5	4.69 x103	4.68	1.3 x103	5.99 x103	9.58 x105	1.1 - 1.7 x108	
Hg	0.027	6.5	0.002	0.48	6.98	1.12 x103	1.5 - 2 x105	
Ni	52.4	1.26 x104	4.1	998	1.36 x104	2.18 x106	2.3 - 3.8 x108	
Pb	0.79	190	0.79	190	380	6.1 x104	0.6 - 2.9 x107	
V	87.4	2.1 x104	14.9	3.6 x103	2.46 x104	3.94 x106	-	
Zn	19.2	4.6 x103	14.0	3.37 x103	8.0 x103	1.28 x106	3.9 - 4.3 x108	
N (as nitrate)	9.2	2.2 x106	not measured		2.2 x106	3.52 x108	4.8 x1010	dissolved only
Si (as reactive silicate)	60	1.45 x107	not measured		1.45 x107	2.32 x109	2.6 x1012	dissolved only
P (as ortho-phosphate)	0.08	1.92 x104	not measured		1.92 x104	3.07 x106	6.0 x109	dissolved only
Total alkanes	84	20.2 kg	30	7.2	27.4	4.38 x103kg	1.5 x106	
Total PAH	16	3.85 kg	5	1.20	5.05 kg	808 kg	0.6 - 1.4 x105	
SPM	-	-	-	-	1153 kg	1.85 x105 kg	2.2 x1011 kg	

a) units are μmol·m^{-3} for metals; mmol·m^{-3} for nutrients; μg·m^{-3} for hydrocarbons; g·m^{-3} for SPM.
b) values obtained by summing the values for all three channels.
c) from Thomas et al. (1983)

5.0 SUGGESTIONS FOR FUTURE SAMPLING

1) The results of this study indicate that the winter chemical composition of the Mackenzie River is similar in different channels and relatively constant from year to year. Estimation of the flow in the Main Channel will give a good approximation of the net flow to the Beaufort Sea and dissolved metal, nutrient and hydrocarbon levels. Future winter studies could be restricted to the Main Channel which is readily accessible by ice road from Inuvik. Particulate concentrations decrease downstream however, so that the particulate flux in the Main Channel will overestimate the net particle flux to the Beaufort Sea by at least 25%. However, the winter particle flux is only a small percentage of the annual total.

2) Further sampling should be focussed on the spring/summer period from early May to late September to characterize the dissolved and suspended particulate chemical load. Concentrations of dissolved metals and hydrocarbons should be lower than winter concentrations for most variables because of higher flows.

3) The Seastar in situ sampler proved to be a reliable means for obtaining time-integrated samples during the winter for particulate hydrocarbons, and some trace metals. Further evaluation is required of the efficiency of both XAD-2 and 8-hydroxyquinoline columns for extraction of dissolved hydrocarbons and trace metals.

4) The Sedisamp continuous-flow centrifuge is the most practical method presently available for obtaining large quantities of suspended particulates for chemical analysis. However, the efficiency of the sampler at low particulate levels is poor.

5) Time series measurements will be important in the summer months because of the highly variable flow in response to storm events in the Mackenzie watershed and possible storm surges in the coastal waters of the Beaufort Sea. Therefore more frequent sampling is recommended (at least monthly).

6) Particle size measurement using a laser based light scattering method appears to be most practical for in the field measurements and approximations of in situ conditions.

7) Suspended particulate concentrations decrease towards the channel mouths. A series of down channel SPM measurements would be useful to quantify this.

8) Water in the various channels appears to be well mixed. It is suggested that sampling effort be concentrated on replication at a single depth and mid-channel location.

9) The dissolved hydrocarbon levels were below detection limits in both bottle samples (18 L) and small in situ sampler volumes (22 to 99 L). However the larger in situ sampler volumes contained hydrocarbons qualitatively similar to those present in the dissolved and the particulate fractions. This indicated that at these detection limits hydrocarbons would be detectable for a total accumulated sample of 200 L or more and quantifiable at 500 L. For hydrocarbons on particulates, a 50 L filtered sample appears adequate for quantification. The substantially larger sample sizes possible with the continuous-flow centrifuge simplifies the sample handling and analysis. However the particulate recovery efficiency must be considered at the prevailing SPM levels to relate concentrations on the sediment to water concentrations. Factors causing compositional differences between particulate collected by filtered and continuous-flow centrifuge should be examined further.

6. LITERATURE CITED

Agemian, H., and R. Thomson, 1980. Simple semi-automated atomic-absorption spectrophotometric method for the determination of arsenic and selenium in fish tissue. Analyst, 105: 902-907.

Andreae, M.O., 1977. Determination of arsenic species in natural waters. Anal. Chem., 49:820-823.

Boehm, P.D., 1981. Petroleum in the marine environment: Physical/Chemical Methods. A background paper submitted to Ocean Sciences Board, National Research Council, National Academy of Sciences, Washington, D.C.

Boyle, E.A., S.S. Huested and B. Grant, 1982. The chemical mass balance of the Amazon Plume - II. Copper, nickel, and cadmium. Deep-Sea Research, 29:1355-1364.

Buckley, D.E. and R.E. Cranston, 1971. Atomic absorption analysis of 18 elements from a single decomposition of aluminosilicate. Chem. Geol., 7:273-284.

Duinker, J.C., R.F. Nolting and H.A. Van Der Sloot, 1979. The determination of suspended metals in coastal waters by different sampling and processing techniques (Filtration and Centrifugation). Netherlands Journal of Sea Research, 13(2):282-297.

Eichelberger, J.W., L.E. Harris and W.L Budde, 1975. Reference compound to calibrate ion abundance measurements in gas chromatography - mass spectrometry. Anal. Chem., 47:995-1000.

Environmental Protection, Northwest Territories District Office, Environment Canada, 1986. A computer database of sediment chemical data for the Beaufort Sea region, contact: District Director, P.O. Box 370, Yellowknife, N.W.T., X1A 2N3, (403) 873-3456.

Erickson, P.E., D. Thomas, R. Pett and B. de Lange Boom, 1983. Issungnak Oceanographic Survey, Part A: Oceanographic properties. A report prepared for Esso Resources Canada Limited, Gulf Canada Resources Inc., Dome Petroleum Limited by Arctic Laboratories Limited, Inuvik, Northwest Territories. 194 pp.

Fletcher, W.K. and D. Polson, 1982. A simple device for sampling shallow waters. Limnol. Oceanogr., 27:188-190.

Forstner, U., and G.T.W. Wittmann, 1979. Metal Pollution in the Aquatic Environment. Springer Verlag, Berlin.

Green, D.R., 1979. Hydrocarbon determination in sea water. A report prepared for the Marine Analytical Chemistry Standards Program by Seakem Oceanography Limited. National Research Council of Canada, Halifax, N.S.

Green, D.R., J.K. Stull and T.C. Heesen, 1986. Determination of chlorinated hydrocarbon in coastal waters using a moored in situ sampler and transplanted live mussels. Marine Pollution Bulletin, 17:324-329.

Hatch, W.R., and W.L. Ott, 1968. Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem., 40:2085-2087.

Hoff, J.T., and D.J. Thomas, 1986. A compilation of statistical analysis of high quality Beaufort Sea sediment data with recommendations for future data collections. A report for Environmental Protection Service, N.W.T. by Arctic Laboratories Limited, 118 pp.

Jansen, P. Ph., L. van Bendegom, J. van den Berg, M. de Vries and A. Zanen, 1979. Principles of River Engineering; The non-tidal alluvial river. Pitman Publishing, London. 507 pp.

Keith, L.H., W. Crummett, J. Deegan, R.A. Libby, J.K. Taylor and G. Wentler, 1983. Principles of Environmental Analysis. Anal. Chem., 55:2210-2218.

Kovat, E., 1981. Z. Anal. Chem., 181:351.

Levinson, A.A., B. Hitchon and S.W. Reeder, 1969. Major element composition of the Mackenzie River at Norman Wells, N.W.T., Canada. Geochimica et Cosmochimica Acta, 33:133-138.

Macdonald, R.W., and F.A. Mclaughlin, 1982. The effect of storage by freezing on dissolved inorganic phosphate, nitrate and reactive silicate for samples from coastal and estuarine waters. Water Res., 16:95-104.

Mackenzie River Basin Committee, 1981. Mackenzie River Basin Study Report. A report under the 1978-81 Federal-Provincial Study Agreement regarding the water and related resources of the Mackenzie River Basin. 231 pp.

Moore, R.M., 1981. Oceanographic distributions of zinc, cadmium, copper and aluminum in waters of the Central Arctic. Geochim. et Cosmochimica. Acta, 45:2475-2482.

Ongley, E.D., 1986. Personal communication of unpublished results.

Ongley, E.D., and D. Blachford, 1982. Application of continuous-flow centrifugation to contaminant analysis of suspended sediment in fluvial systems. Environ. Techno. Letters, 3:219-228.

Reeder, S.W., B. Hitchon and A.A. Levinson, 1972. Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada I - Factors controlling inorganic composition. Geochim. et Cosmochimica. Acta, 36:825-865.

Sokal, R.R., and R.J. Rohlf, 1969. Biometry: The Principles and Practice of Statistics in Biological Research, Freeman and Co., San Francisco. 370 pp.

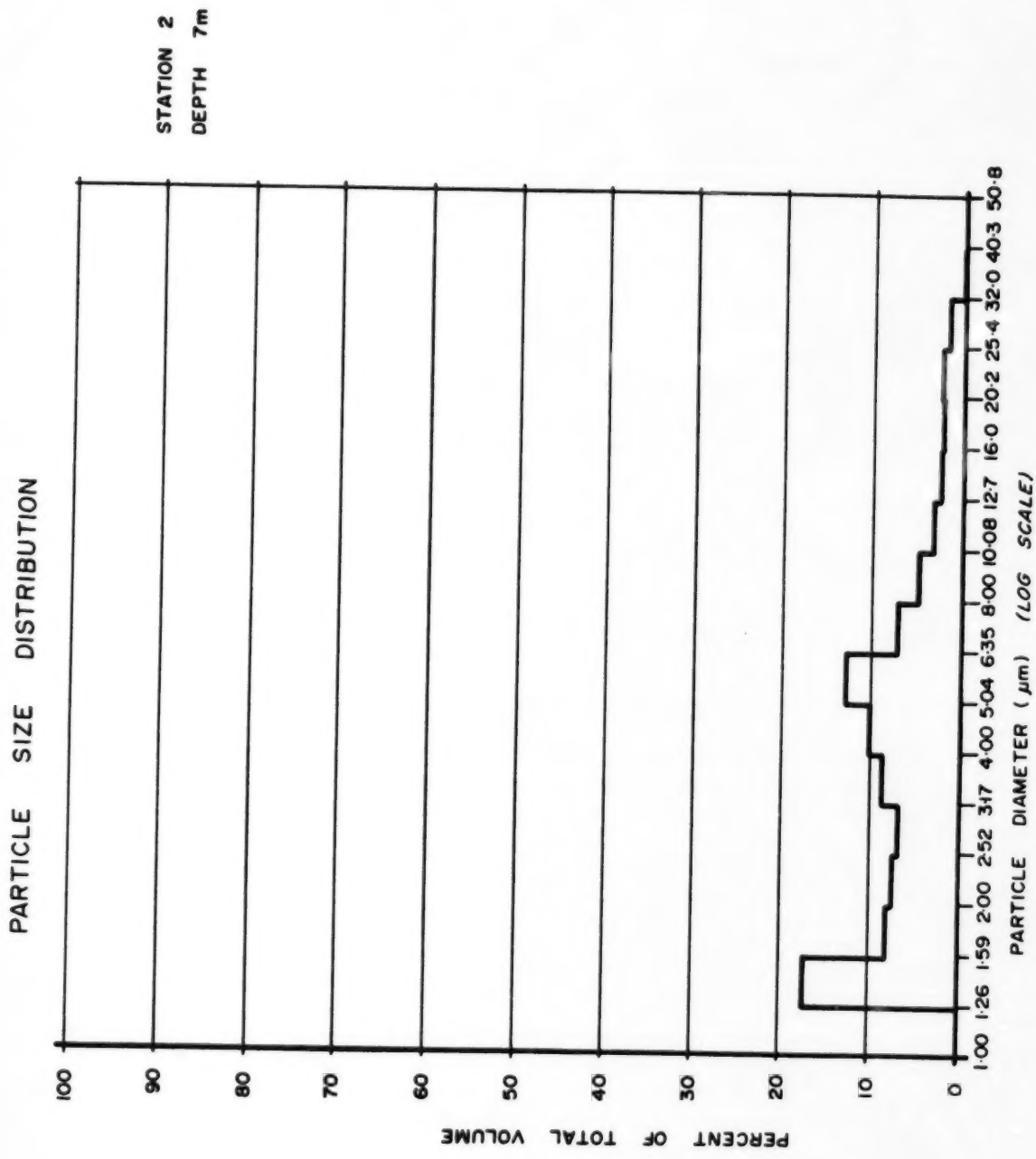
Thomas, D.J., R.W. Macdonald and A.B. Cornford, 1983. A comparison of natural and petroleum resource development related fluxes of metals, hydrocarbons, and nitrogenphosphorus and silicon to the Beaufort Sea. Can. Tech. Rep. Hydrogr. Ocean Sci. No. 30, 48 pp.

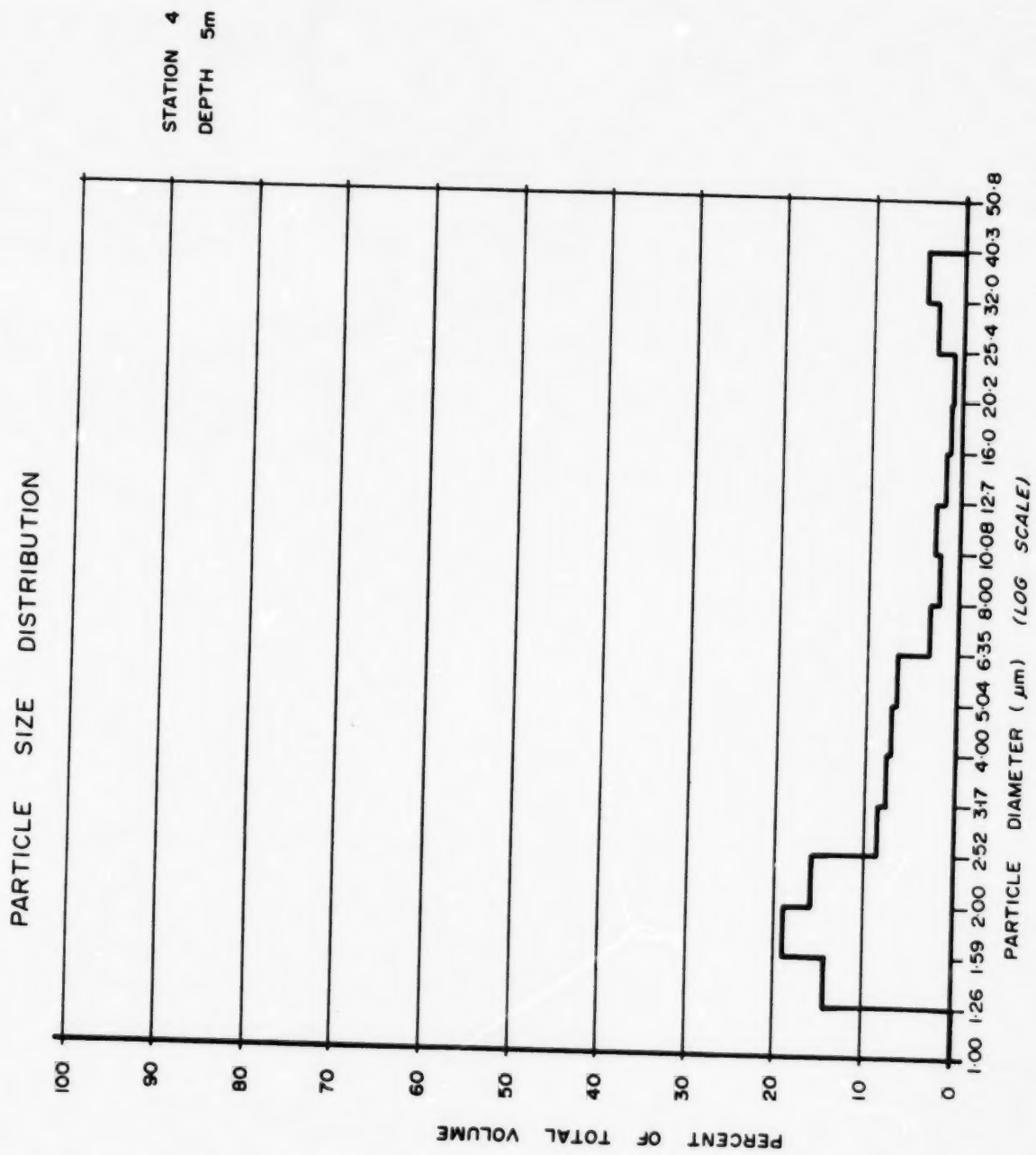
APPENDIX A.

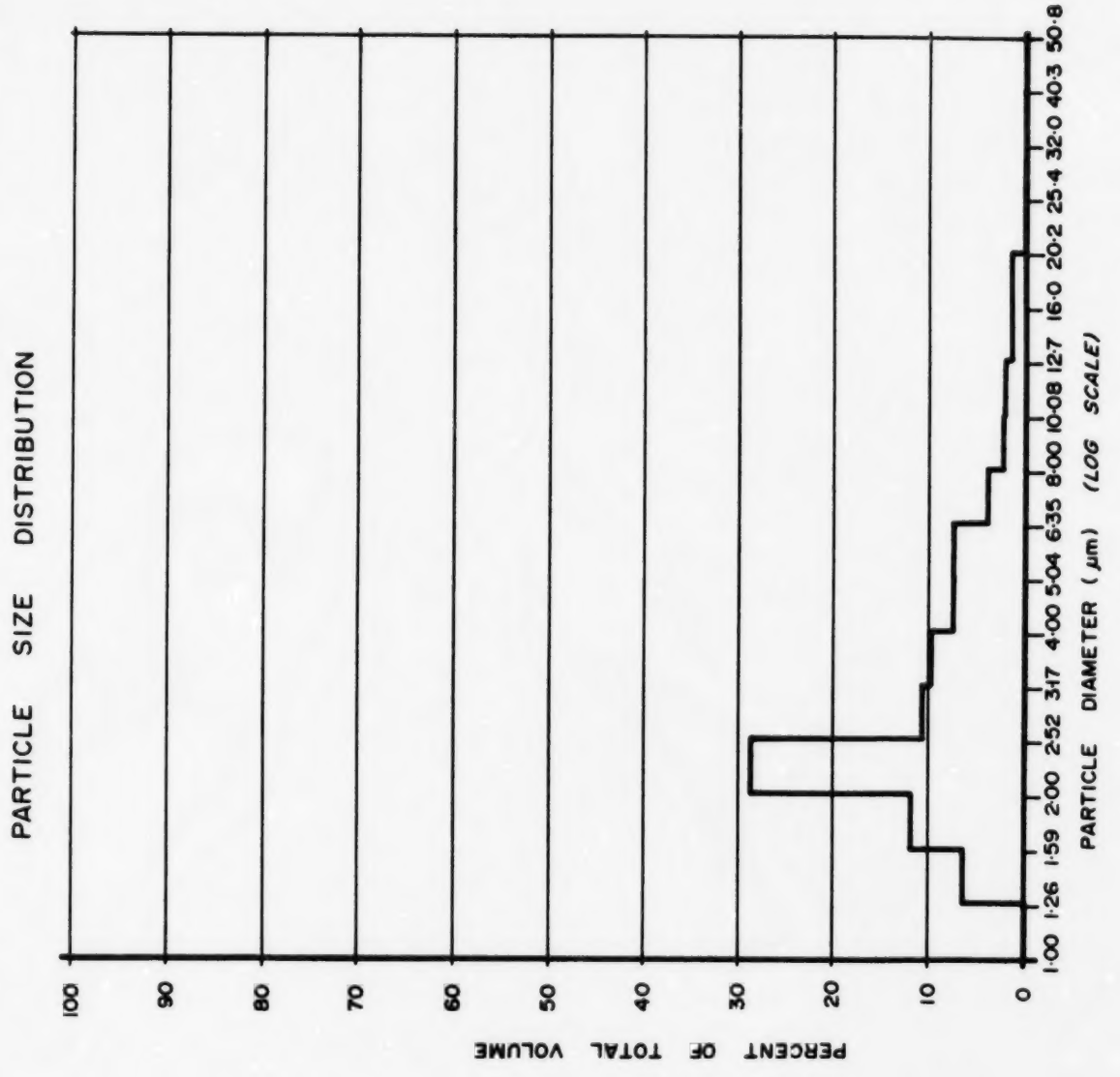
Coulter Counter Analysis of Suspended Particulates East Channel, April 1985

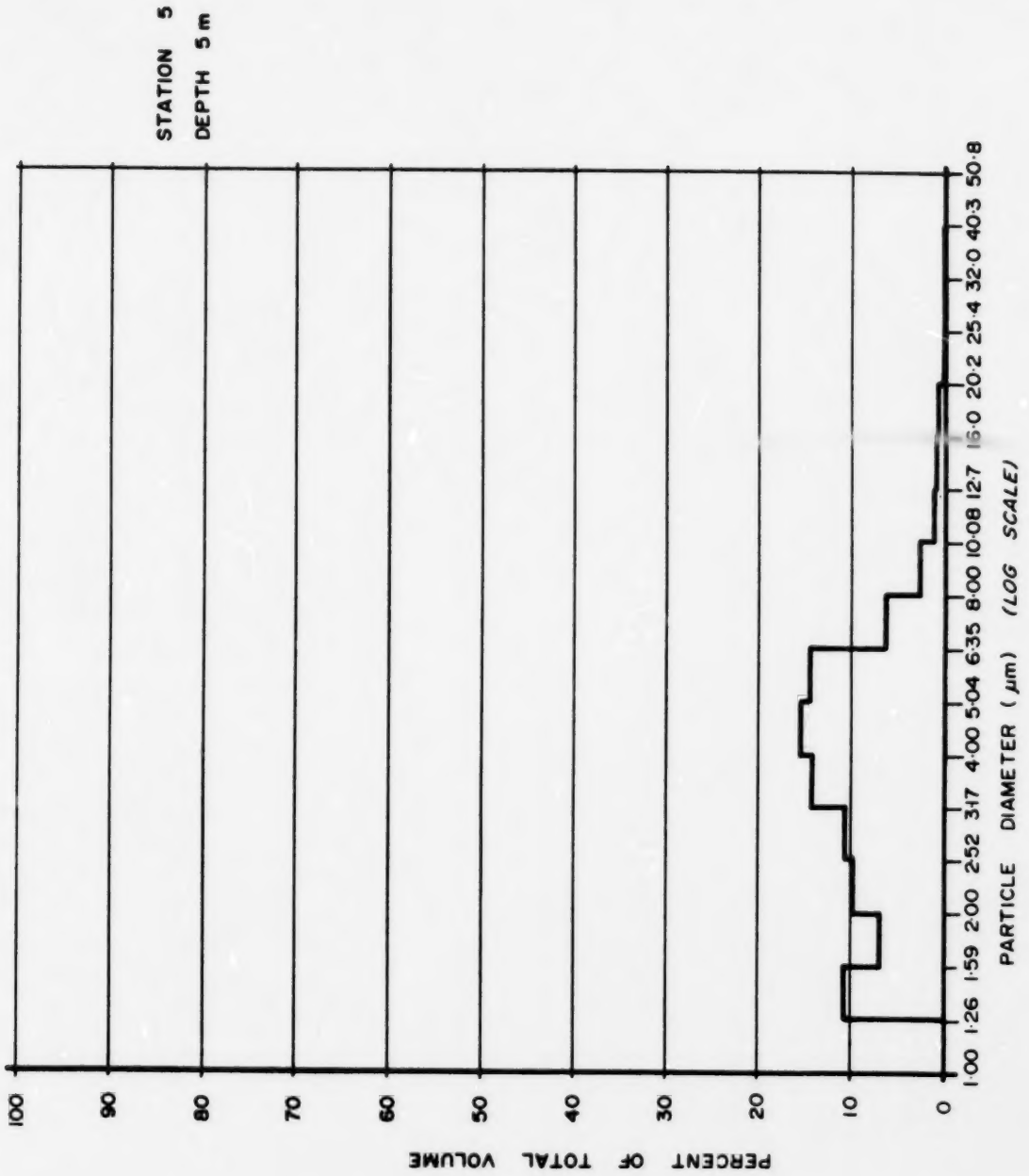
Histograms of percent total volume of particulates vs particle diameter plots;

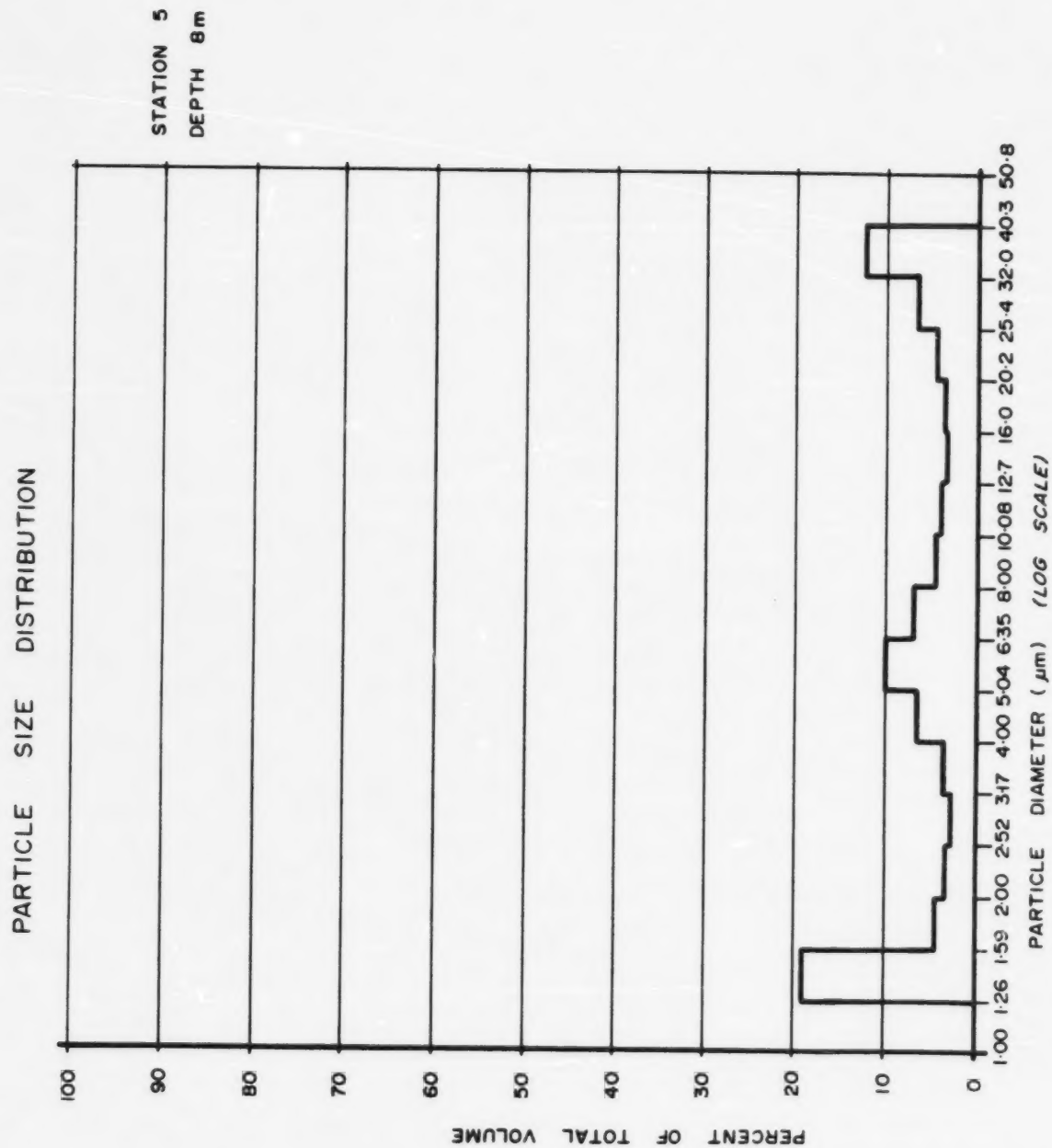
a) Station 2, 7 m
b) Station 4, 5 m
c) Station 5, 2 m
d) Station 5, 5 m
e) Station 5, 8 m
f) Station 6, 5 m
g) Station 8, 5 m

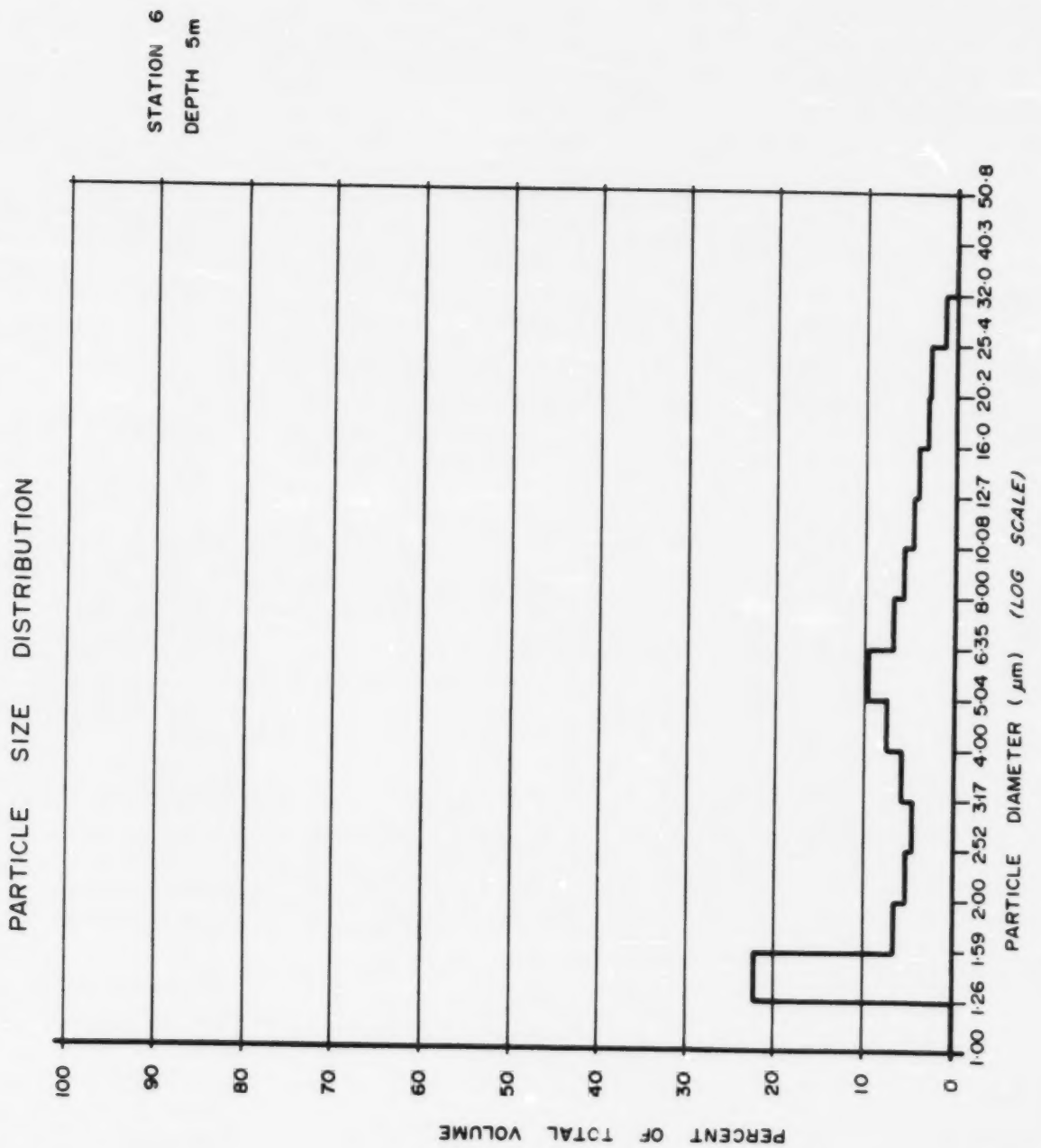

PARTICLE SIZE DISTRIBUTION
STATION 2
DEPTH 7m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)

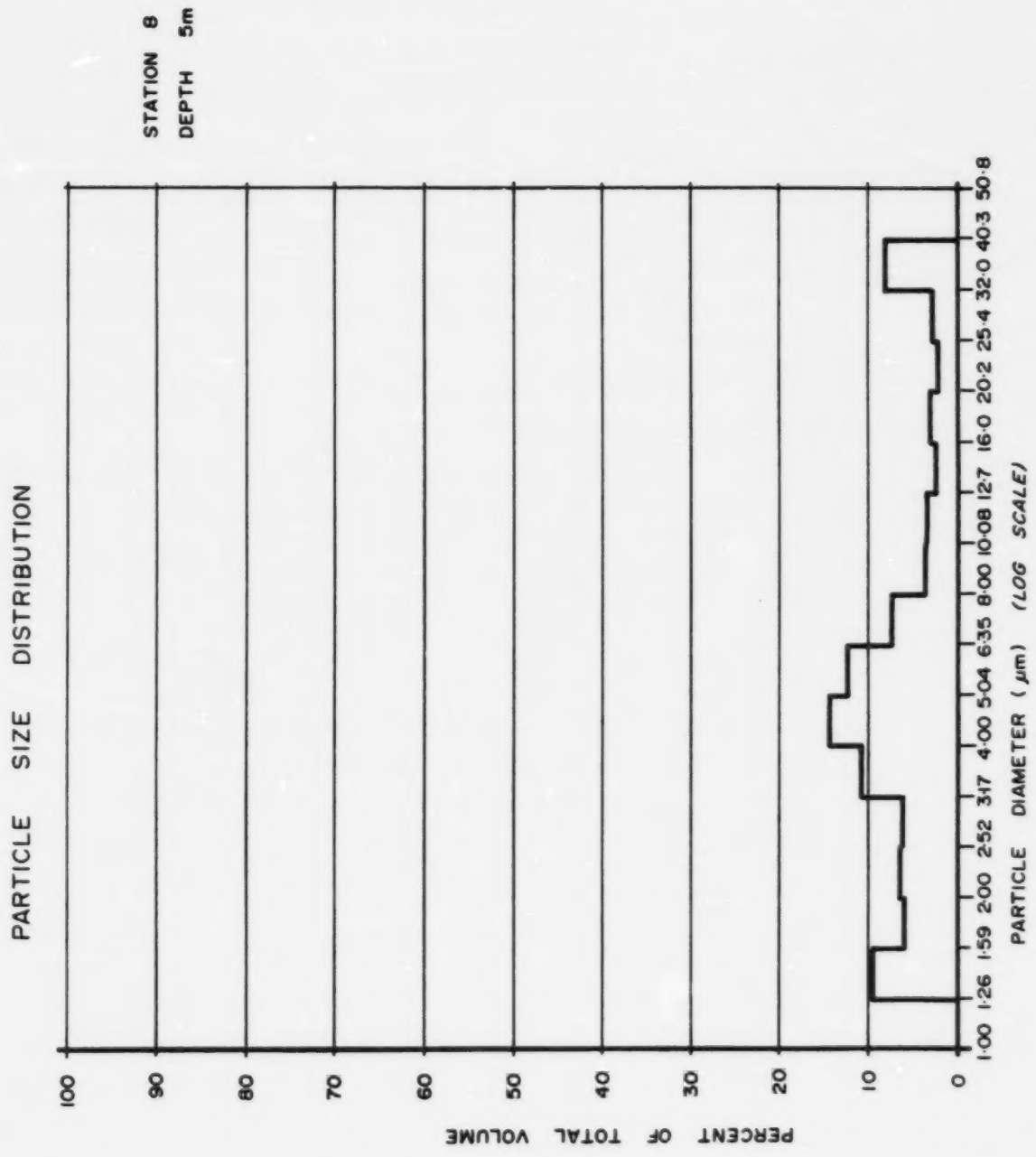

PARTICLE SIZE DISTRIBUTION
STATION 4
DEPTH 5m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)


PARTICLE SIZE DISTRIBUTION
STATION 5
DEPTH 2m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)


PARTICLE SIZE DISTRIBUTION
STATION 5
DEPTH 5 m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)


PARTICLE SIZE DISTRIBUTION
STATION 5
DEPTH 8m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)


PARTICLE SIZE DISTRIBUTION
STATION 6
DEPTH 5m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)


PARTICLE SIZE DISTRIBUTION
STATION 8
DEPTH 5m
PERCENT OF TOTAL VOLUME
100
90
80
70
60
50
40
30
20
10
0
1·00 1·26 1·59 2·00 2·52 3·17 4·00 5·04 6·35 8·00 10·08 12·7 16·0 20·2 25·4 32·0 40·3 50·8
PARTICLE DIAMETER (μm) (LOG SCALE)

APPENDIX B.

Representative Particle Size Distributions by HIAC/ROYCO Analyser for Middle, Reindeer, Main and East Channels, February, 1986

1) CMH 150 sensor head (done within 24 h of collection).
2) 346 BCL sensor head (after 6 weeks storage).
3) Calibration with 5.0 µm, 10.0 µm and 20.0 µm particles, CMH 150 sensor

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: MID E B-2 SENSOR: CMH 150 OPER: P DATE: 030286

RANGE: 45 THRESH: B DIA(1): 3.0 p(Y1): 1 p(Y2): 1

EXPdY1: 1.0 EXPd50: 1.0 EXPdY2: 1.0 TOLdY1: 1 TOLd50: 1 TOLdY2: 1

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1308	2236	1954	1308	1374	744	482	304	154	68	33	13
	11	5	3	1	1	1	0	0	0	0	0	1
2	1353	2255	1873	1362	1361	745	472	311	146	65	19	13
	17	2	6	0	2	0	0	0	0	0	0	1
3	1330	2228	1988	1411	1361	727	445	265	133	61	22	17
	5	3	2	2	1	0	1	0	0	0	0	0

						POPULATION				VOLUME		
ANALYSIS	i	d(i)	AVG	BKG	CPC	%DIF	SD	%<	%>	%DIF	%<	%>
	1	3.3	1330	---	1330	13.30	0.22	13.30	100.00	1.42	1.42	100.00
	2	3.9	2240	---	2240	22.39	0.14	35.70	86.70	3.93	5.35	98.58
	3	4.6	1938	---	1938	19.38	0.59	55.08	64.30	5.58	10.93	94.65
	4	5.4	1360	---	1360	13.60	0.51	68.68	44.92	6.44	17.37	89.07
	5	6.3	1365	---	1365	13.65	0.08	82.33	31.32	10.62	27.99	82.63
	6	7.5	739	---	739	7.39	0.10	89.72	17.67	9.44	37.43	72.01
	7	8.8	466	---	466	4.66	0.19	94.38	10.28	9.79	47.22	62.57
	8	10.4	293	---	293	2.93	0.25	97.31	5.62	10.12	57.33	52.78
	9	12.3	144	---	144	1.44	0.11	98.75	2.69	8.18	65.51	42.67
	10	14.5	65	---	65	0.65	0.04	99.40	1.25	6.02	71.53	34.49
	11	17.1	25	---	25	0.25	0.07	99.65	0.60	3.77	75.31	28.47
	12	20.2	14	---	14	0.14	0.02	99.79	0.35	3.60	78.91	24.69
	13	23.8	11	---	11	0.11	0.06	99.90	0.21	4.54	83.45	21.09
	14	28.1	3	---	3	0.03	0.02	99.93	0.10	2.26	85.71	16.55

B-2

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: R C 10M SENSOR: CMH 150 OPER: PAUL DATE: 040286

RANGE: 45 THRESH: B DIA(1): 3.0 p(Y1): 1 p(Y2): 1

EXPd(1): 1.0 EXPd50: 1.0 EXPdY2: 1.0 TOLdY1: 1 TOLd50: 1 TOLdY2: 1

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1354	2066	1849	1580	1340	757	544	269	121	65	26	16
	6	3	2	0	1	0	0	0	0	0	0	1
2	1279	2131	2017	1527	1319	743	486	243	147	51	26	18
	4	4	2	2	1	0	0	0	0	0	0	1
3	1329	2099	1945	1508	1277	763	530	280	130	90	26	11
	5	5	1	1	0	0	1	0	1	0	0	0

						POPULATION				VOLUME		
ANALYSIS	i	d(i)	AVG	BKG	CPC	%DIF	SD	%<	%>	%DIF	%<	%>
	1	3.3	1321	---	1321	13.21	0.38	13.21	100.00	1.41	1.41	100.00
	2	3.9	2099	---	2099	20.99	0.32	34.19	86.79	3.68	5.09	98.59
	3	4.6	1937	---	1937	19.37	0.84	53.56	65.81	5.58	10.67	94.91
	4	5.4	1538	---	1538	15.38	0.38	68.94	46.44	7.28	17.96	89.33
	5	6.3	1312	---	1312	13.12	0.32	82.06	31.06	10.21	28.16	82.04
	6	7.5	754	---	754	7.54	0.10	89.61	17.94	9.64	37.81	71.84
	7	8.8	520	---	520	5.20	0.30	94.81	10.39	10.92	48.73	62.19
	8	10.4	264	---	264	2.64	0.19	97.45	5.19	9.11	57.84	51.27
	9	12.3	133	---	133	1.33	0.13	98.77	2.55	7.52	65.36	42.17
	10	14.5	69	---	69	0.69	0.20	99.46	1.23	6.40	71.75	34.64
	11	17.1	26	---	26	0.26	0.00	99.72	0.54	3.98	75.73	28.25
	12	20.2	15	---	15	0.15	0.04	99.87	0.28	3.77	79.50	24.27
	13	23.8	5	---	5	0.05	0.01	99.92	0.13	2.07	81.57	20.50
	14	28.1	4	---	4	.04	0.01	99.96	0.08	2.71	84.2	18.43

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: MAIN C 10M SENSOR: CMH 150 OPER: PAUL DATE: 060286

RANGE: 45 THRESH: 8 DIA(1): 3.0 p(Y1): 1 p(Y2): 1

EXPdY1: 1.0 EXPd50: 1.0 EXPdY2: 1.0 TOLdY1: 1 TOLd50: 1 TOLdY2: 1

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1040	2153	1771	1256	1391	872	639	395	219	125	69	45
	15	6	1	0	1	1	0	0	0	0	0	1
2	1017	2138	1790	1214	1464	876	586	425	224	137	59	39
	20	8	2	1	0	0	0	0	0	0	0	1
3	1081	2130	1823	1261	1419	849	577	399	227	119	55	34
	18	1	3	1	2	1	0	0	0	0	0	0
4	1110	2083	1766	1311	1402	876	608	394	210	115	60	41
	13	7	2	1	0	0	1	0	0	0	0	0
5	1078	2189	1796	1295	1463	846	550	361	220	96	58	24
	16	4	4	0	2	0	0	0	0	0	0	0

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION ZDIF	POPULATION SD	POPULATION %S	POPULATION %>	VOLUME ZDIF	VOLUME %S	VOLUME %>
	1	3.3	1065	---	1065	10.65	0.37	10.65	100.00	0.90	0.90	100.00
	2	3.9	2139	---	2139	21.39	0.38	32.04	89.35	2.96	3.85	99.10
	3	4.6	1789	---	1789	17.89	0.23	49.93	67.96	4.06	7.92	96.15
	4	5.4	1267	---	1267	12.67	0.38	62.60	50.07	4.73	12.65	92.08
	5	6.3	1428	---	1428	14.28	0.34	76.88	37.40	8.76	21.41	87.35
	6	7.5	864	---	864	8.64	0.15	85.52	23.12	8.70	30.11	78.60
	7	8.8	592	---	592	5.92	0.34	91.44	14.48	9.80	39.91	69.89
	8	10.4	395	---	395	3.95	0.23	95.39	8.56	10.74	50.65	60.09
	9	12.3	220	---	220	2.20	0.06	97.59	4.61	9.83	60.48	49.35
	10	14.5	118	---	118	1.18	0.15	98.77	2.41	8.69	69.17	39.52
	11	17.1	60	---	60	0.60	0.05	99.37	1.23	7.26	76.43	30.83
	12	20.2	37	---	37	.37	0.08	99.74	0.63	7.25	83.[illegible]	23.57
	13	23.8	16	---	16	0.16	0.03	99.90	0.26	5.34	89.0[illegible]	16.31

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: EAST C BM SENSOR: CNH 150 OPER: PAUL DATE: 080286

RANGE: 45 THRESH: 8 DIA(1): 3.0 p(Y1): 1 p(Y2): 1

EXPdY1: 1.0 EXPd50: 1.0 EXPdY2: 1.0 TOLdY1: 1 TOLd50: 1 TOLdY2: 1

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1180	2279	1916	1304	1416	876	506	291	127	55	25	13
	8	4	0	0	0	0	0	0	0	0	0	1
2	1181	2338	1969	1297	1450	752	498	267	144	71	20	7
	3	2	0	0	0	0	1	0	0	0	0	0
3	1218	2391	1881	1346	1391	737	523	257	146	61	31	11
	3	2	0	0	1	0	0	1	0	0	0	0
4	1209	2340	1851	1335	1394	833	512	290	134	54	30	8
	5	4	0	0	0	1	0	0	0	0	0	0
5	1245	2413	1904	1284	1406	776	492	285	106	61	15	7
	2	2	1	0	0	0	0	0	0	1	0	0

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION %DIF	POPULATION SD	POPULATION %<	POPULATION %>	VOLUME %DIF	VOLUME %<	VOLUME %>
	1	3.3	1207	---	1207	12.07	0.27	12.07	100.00	1.36	1.36	100.00
	2	3.9	2352	---	2352	23.52	0.52	35.59	87.93	4.36	5.73	98.64
	3	4.6	1904	---	1904	19.04	0.44	54.63	64.41	5.81	11.53	94.27
	4	5.4	1313	---	1313	13.13	0.26	67.76	45.37	6.58	18.11	88.47
	5	6.3	1411	---	1411	14.11	0.24	81.88	32.24	11.62	29.73	81.89
	6	7.5	795	---	795	7.95	0.58	89.82	18.12	10.75	40.48	70.27
	7	8.8	506	---	506	5.06	0.12	94.89	10.18	11.25	51.72	59.53
	8	10.4	278	---	278	2.78	0.15	97.67	5.11	10.15	61.87	48.28
	9	12.3	131	---	131	1.31	0.16	98.98	2.33	7.88	69.75	38.13
	10	14.5	60	---	60	0.60	0.07	99.58	1.02	5.95	75.70	30.25
	11	17.1	24	---	24	0.24	0.07	99.83	0.42	3.92	79.62	24.30
	12	20.2	9	---	9	0.09	0.03	99.92	0.17	2.45	82.07	20.38
	13	23.8	4	---	4	0.04	0.02	99.96	0.08	1.84	83.90	17.93
	14	28.1	3	---	3	.03	0.01	99.99	0.04	2.01	85.[illegible]	16.10

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: ARTIC MID C-10-2 10M SENSOR: 346 BCL OPER: MILLER DATE: 3 18 86

RANGE: 45 THRESH: A DIA(1): 0.4 p(Y1): 10 p(Y2): 90

EXPdY1: N/A EXPd50: N/A EXPdY2: N/A TOLdY1: 0 TOLd50: 0 TOLdY2: 0

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	27	70	164	153	152	207	134	85	146	186	298	412
	625	886	1306	1505	1724	1708	1370	681	349	211	110	45

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION INCR	POPULATION SD	POPULATION %S	POPULATION %2	VOLUME INCR	VOLUME %S	VOLUME %2
	1	0.4	27	0	27	0.22	---	0.22	100.00	0.00	0.00	100.00
	2	0.5	70	0	70	0.56	---	0.78	99.78	0.00	0.00	100.00
	3	0.6	164	0	164	1.31	---	2.09	99.23	0.00	0.00	100.00
	4	0.7	153	0	153	1.22	---	3.31	97.91	0.00	0.00	100.00
	5	0.8	152	0	152	1.22	---	4.52	96.69	0.00	0.00	100.00
	6	1.0	207	0	207	1.65	---	6.18	95.48	0.00	0.01	100.00
	7	1.2	134	0	134	1.07	---	7.25	93.82	0.00	0.01	99.99
	8	1.4	85	0	85	0.68	---	7.93	92.75	0.00	0.02	99.99
	9	1.6	146	0	146	1.17	---	9.10	92.07	0.01	0.03	99.98
	10	1.9	186	0	186	1.49	---	10.58	90.90	0.03	0.06	99.97
	11	2.3	298	0	298	2.38	---	12.97	89.42	0.07	0.13	99.94
	12	2.7	412	0	412	3.29	---	16.26	87.03	0.17	0.30	99.87
	13	3.2	625	0	625	5.00	---	21.26	83.74	0.42	0.73	99.70
	14	3.7	886	0	886	7.08	---	28.34	78.74	0.99	1.72	99.27

SAMPLE: ARTIC MID C-10-2 10M

15	4.4	1306	0	1306	10.44	---	38.78	71.66	2.39	4.11	98.28
16	5.2	1505	0	1505	12.03	---	50.81	61.22	4.53	8.64	95.89
17	6.2	1724	0	1724	13.78	---	64.59	49.19	8.52	17.16	91.36
18	7.3	1708	0	1708	13.65	---	78.25	35.41	13.87	31.03	82.84
19	8.6	1370	0	1370	10.95	---	89.20	21.75	18.28	49.31	68.97
20	10.1	681	0	681	5.44	---	94.64	10.80	14.93	64.24	50.69
21	11.9	349	0	349	2.79	---	97.43	5.36	12.57	76.82	35.76
22	14.1	211	0	211	1.69	---	99.12	2.57	12.49	89.30	23.18
23	16.6	110	0	110	0.88	---	100.00	0.88	10.70	100.00	10.70
24	OSD	45	0	45							

12,554 /10mL

SUMMARY	MEAN.VG	d(Y1).VG	d(50).VG	d(Y2).VG	d(50/Y1)	d(Y2/50)
POP	5.8	2.0	5.7	9.5	2.84	1.69
VOL	10.1	5.9	9.4	15.4	1.60	1.64
FLAG						

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: ARTIC RC-4-1 10ML SENSOR: 346 BCL OPER: MILLER DATE: 3 18 86

RANGE: 45 THRESH: A DIA(1): 0.4 p(Y1): 10 p(Y2): 90

EXPd(1): N/A EXPd50: N/A EXPdY2: N/A TOLdY1: 0 TOLd50: 0 TOLdY2: 0

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	357	612	1066	904	1007	1162	749	710	1016	1346	1737	2370
	2711	3077	3277	2872	2474	1869	1453	776	409	309	169	43

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION INDIF	POPULATION SD	POPULATION %<	POPULATION %>	VOLUME INDIF	VOLUME %<	VOLUME %>
	1	0.4	357	0	357	1.10	---	1.10	100.00	0.00	0.00	100.00
	2	0.5	612	0	612	1.89	---	2.99	98.90	0.00	0.00	100.00
	3	0.6	1066	0	1066	3.29	---	6.27	97.01	0.00	0.01	100.00
	4	0.7	904	0	904	2.79	---	9.06	93.73	0.01	0.01	100.00
	5	0.8	1007	0	1007	3.10	---	12.17	90.94	0.01	0.02	99.99
	6	1.0	1162	0	1162	3.58	---	15.75	87.83	0.02	0.04	99.98
	7	1.2	749	0	749	2.31	---	18.06	84.25	0.02	0.06	99.96
	8	1.4	710	0	710	2.19	---	20.25	81.94	0.03	0.09	99.94
	9	1.6	1016	0	1016	3.13	---	23.38	79.75	0.07	0.16	99.91
	10	1.9	1346	0	1346	4.15	---	27.53	76.62	0.15	0.31	99.84
	11	2.3	1737	0	1737	5.36	---	32.89	72.47	0.32	0.63	99.69
	12	2.7	2370	0	2370	7.31	---	40.19	67.11	0.72	1.36	99.37
	13	3.2	2711	0	2711	8.36	---	48.55	59.81	1.36	2.72	98.64
	14	3.7	3077	0	3077	9.49	---	58.04	51.45	2.54	5.26	97.28

SAMPLE: ARTIC RC-4-1 10ML

	15	4.4	3277	0	3277	10.10	---	68.15	41.96	4.44	9.71	94.74
	16	5.2	2872	0	2872	8.86	---	77.00	31.86	6.40	16.11	90.30
	17	6.2	2474	0	2474	7.63	---	84.63	23.00	9.06	25.16	83.89
	18	7.3	1869	0	1869	5.76	---	90.39	15.37	11.24	36.41	74.84
	19	8.6	1453	0	1453	4.48	---	94.87	9.61	14.36	50.77	63.59
	20	10.1	776	0	776	2.39	---	97.26	5.13	12.60	63.37	49.23
	21	11.9	409	0	409	1.26	---	98.53	2.74	10.91	74.28	36.63
	22	14.1	309	0	309	0.95	---	99.48	1.47	13.55	87.83	25.72
	23	16.6	169	0	169	0.52	---	100.00	0.52	12.17	100.00	12.17
	24	OSD	43	0	43							
			32,475									

SUMMARY	MEAN.UM	d(Y1).UM	d(50).UM	d(Y2).UM	d(50/Y1)	d(Y2/50)
POP	4.0	0.8	3.6	7.9	4.32	2.20
VOL	9.8	4.9	9.3	15.8	1.91	1.71
FLAG						

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HIAC PARTICLE SIZE ANALYSIS

SAMPLE: ARTIC HC5 10ML SENSOR: 346 BCL OPER: MILLER DATE: 3 18 86

RANGE: 45 THRESH: A DIA(1): 0.4 p(Y1): 10 p(Y2): 90

EXPdY1: N/A EXPd50: N/A EXPdY2: N/A TOLdY1: 0 TOLd50: 0 TOLdY2: 0

Date	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1080	2587	6132	6343	7137	8579	2903	3244	3649	4149	4365	4354
	3976	3047	2038	1276	758	390	219	78	31	31	17	4

						POPULATION				VOLUME			
ANALYSIS	i	d(i)	AVG	BKG	CPC	%DIF	SD	%<	%>	%DIF	%<	%>
	1	0.4	1080	0	1080	1.63	---	1.63	100.00	0.01	0.01	100.00
	2	0.5	2587	0	2587	3.90	---	5.52	98.37	0.02	0.03	99.99
	3	0.6	6132	0	6132	9.24	---	14.76	94.48	0.08	0.11	99.97
	4	0.7	6343	0	6343	9.56	---	24.32	85.24	0.14	0.26	99.89
	5	0.8	7137	0	7137	10.75	---	35.07	75.68	0.27	0.52	99.75
	6	1.0	8579	0	8579	12.92	---	47.99	64.93	0.52	1.05	99.48
	7	1.2	2903	0	2903	4.37	---	52.36	52.01	0.29	1.34	98.95
	8	1.4	3244	0	3244	4.89	---	57.25	47.64	0.54	1.87	98.66
	9	1.6	3649	0	3649	5.50	---	62.75	42.75	0.99	2.86	98.13
	10	1.9	4149	0	4149	6.25	---	69.00	37.25	1.85	4.71	97.14
	11	2.3	4365	0	4365	6.58	---	75.57	31.00	3.20	7.91	95.29
	12	2.7	4354	0	4354	6.56	---	82.13	24.43	5.24	13.14	92.09
	13	3.2	3976	0	3976	5.99	---	88.12	17.87	7.86	21.00	86.86
	14	3.7	3047	0	3047	4.59	---	92.71	11.88	9.89	30.89	79.00
SAMPLE: ARTIC HC5 10ML												
	15	4.4	2038	0	2038	3.07	---	95.78	7.29	10.87	41.77	69.11
	16	5.2	1276	0	1276	1.92	---	97.70	4.22	11.18	52.95	58.23
	17	6.2	758	0	758	1.14	---	98.85	2.30	10.92	63.87	47.05
	18	7.3	390	0	390	0.59	---	99.43	1.15	9.23	73.09	36.14
	19	8.6	219	0	219	0.33	---	99.76	0.57	8.51	81.61	26.91
	20	10.1	78	0	78	0.12	---	99.88	0.24	4.98	86.59	18.39
	21	11.9	31	0	31	0.05	---	99.93	0.12	3.25	89.84	13.41
	22	14.1	31	0	31	0.05	---	99.97	0.07	5.34	95.18	10.16
	23	16.6	17	0	17	0.03	---	100.00	0.03	4.82	100.00	4.82
	24	OSD	4	0	4							

SUMMARY	MEAN,um	d(Y1),um	d(50),um	d(Y2),um	d(50/Y1)	d(Y2/50)
POP	1.8	0.6	1.2	3.7	1.89	3.19
VOL	6.5	2.7	5.4	13.1	2.04	2.41
FLAG						

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HIAC PARTICLE SIZE ANALYSIS

SAMPLE: ARTIC EC3 10ML SENSOR: 346 BCL OPER: MILLER DATE: 3 18 86

RANGE: 45 THRESH: A DIA(1): 0.4 p(Y1): 10 p(Y2): 90

ExPd(1): N/A ExPd50: N/A EXPdY2: N/A TOLdY1: 0 TOLd50: 0 TOLdY2: 0

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	13	28	65	50	41	45	33	40	33	60	81	123
	185	288	485	638	890	1000	1019	517	247	137	46	7

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION IDIF	POPULATION SD	POPULATION %<	POPULATION %>	VOLUME IDIF	VOLUME %<	VOLUME %>
	1	0.4	13	0	13	0.21	---	0.21	100.00	0.00	0.00	100.00
	2	0.5	28	0	28	0.46	---	0.68	99.79	0.00	0.00	100.00
	3	0.6	65	0	65	1.07	---	1.75	99.32	0.00	0.00	100.00
	4	0.7	50	0	50	0.82	---	2.57	98.25	0.00	0.00	100.00
	5	0.8	41	0	41	0.68	---	3.25	97.43	0.00	0.00	100.00
	6	1.0	45	0	45	0.74	---	3.99	96.75	0.00	0.00	100.00
	7	1.2	33	0	33	0.54	---	4.53	96.01	0.00	0.01	100.00
	8	1.4	40	0	40	0.66	---	5.19	95.47	0.00	0.01	100.00
	9	1.6	33	0	33	0.54	---	5.74	94.81	0.00	0.01	99.99
	10	1.9	60	0	60	0.99	---	6.73	94.26	0.01	0.03	99.99
	11	2.3	81	0	81	1.34	---	8.06	93.27	0.03	0.06	99.97
	12	2.7	123	0	123	2.03	---	10.09	91.94	0.08	0.14	99.94
	13	3.2	185	0	185	3.05	---	13.14	89.91	0.20	0.34	99.86
	14	3.7	288	0	288	4.75	---	17.89	86.86	0.52	0.86	99.66

SAMPLE: ARTIC EC3 10ML

15	4.4	485	0	485	8.00	---	25.89	82.11	1.43	2.29	99.14
16	5.2	638	0	638	10.52	---	36.41	74.11	3.08	5.37	97.71
17	6.2	890	0	890	14.68	---	51.09	63.59	7.06	12.43	94.63
18	7.3	1000	0	1000	16.49	---	67.58	48.91	13.04	25.48	87.57
19	8.6	1019	0	1019	16.80	---	84.38	32.42	21.83	47.31	74.53
20	10.1	517	0	517	8.53	---	92.91	15.62	18.20	65.51	52.69
21	11.9	247	0	247	4.07	---	96.98	7.09	14.29	79.80	34.49
22	14.1	137	0	137	2.26	---	99.24	3.02	13.02	92.82	20.20
23	16.6	46	0	46	0.76	---	100.00	0.76	7.18	100.00	7.18
24	OSD	7	0	7							
		6071									

SUMMARY	MEAN.VG	d(Y1).VG	d(50).VG	d(Y2).VG	d(50/Y1)	d(Y2/50)
POP	6.7	2.9	6.7	10.3	2.29	1.54
VOL	10.1	6.4	9.5	14.7	1.48	1.54
FLAG						

HIAC PARTICLE SIZE ANALYSIS

SAMPLE: STD 5, 10, 20 AND 43 SENSOR: CMH 150 OPER: PAUL DATE: 060286

RANGE: 45 THRESH: 8 DIA(1): 3.0 p(Y1): 1 p(Y2): 1

EXPdY1: 1.0 EXPd50: 1.0 EXPdY2: 1.0 TOLdY1: 1 TOLd50: 1 TOLdY2: 1

DATA	1/13	2/14	3/15	4/16	5/17	6/18	7/19	8/20	9/21	10/22	11/23	12/24
1	1443	2846	1187	328	481	134	875	820	123	46	58	1282
	42	9	2	239	83	1	0	0	0	0	0	1
2	1478	2813	1213	341	502	127	889	834	112	40	52	1237
	40	9	2	236	74	2	0	0	0	0	0	1
3	1361	2933	1268	346	508	111	755	868	119	41	61	1265
	44	13	1	215	89	3	0	1	0	0	0	0

ANALYSIS	i	d(i)	AVG	BKG	CPC	POPULATION %DIF	POPULATION SD	POPULATION %≤	POPULATION %≥	VOLUME %DIF	VOLUME %≤	VOLUME %≥
	1	3.3	1427	---	1427	14.27	0.60	14.27	100.00	0.14	0.14	100.00
	2	3.9	2864	---	2864	28.64	0.62	42.91	85.73	0.45	0.59	99.86
	3	4.6	1223	---	1223	12.23	0.41	55.14	57.09	0.32	0.91	99.41
	4	5.4	338	---	338	3.38	0.09	58.52	44.86	0.14	1.05	99.09
	5	6.3	497	---	497	4.97	0.14	63.49	41.48	0.35	1.40	98.95
	6	7.5	124	---	124	1.24	0.12	64.73	36.51	0.14	1.54	98.60
	7	8.8	840	---	840	8.40	0.74	73.13	35.27	1.59	3.13	98.46
	8	10.4	841	---	841	8.41	0.25	81.53	26.87	2.62	5.75	96.87
	9	12.3	118	---	118	1.18	0.06	82.71	18.47	0.60	6.35	94.25
	10	14.5	42	---	42	0.42	0.03	83.14	17.29	0.36	6.71	93.65
	11	17.1	57	---	57	0.57	0.05	83.71	16.87	0.79	7.49	93.29
	12	20.2	1261	---	1261	12.61	0.23	96.32	16.30	28.60	36.09	92.51
	13	23.8	42	---	42	0.42	0.02	96.74	3.68	1.56	37.65	63.91
	14	28.1	10	---	10	0.10	0.02	96.84	3.26	0.63	38.29	62.35